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A STUDY OF THE CHEMICAL COMPONENTS OF *DECALEPIS HAMILTONII (MAKALI VERU)*

Part IV. Resinols of *Decalepis Hamiltonii* and *Hemidesmus indicus*

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In Part I[1] it was shown that the petroleum ether extract of the *Decalepis* roots contained a ketonic substance melting at 83°, resinol fractions melting between 130° and 185°, a definite compound of the same group melting at 235–36°, sterols and *para*-methoxysalicylicaldehyde. The term resinol was used to indicate tentatively substances which were alcoholic in nature and which did not give the correct reactions of sterols and its use was justified by their similarity with substances of the type of amyrin. Their chemical composition approximated closely to the formula $C_{30}H_{50}O$. They gave a pink colour with Liebermann-Burchard reagent and a yellow solution with green fluorescence in Salkowski's reaction. Their exact nature has now been investigated.

As already described[1] the alcohol-soluble portion of the petroleum ether extract was separated into three fractions and from the middle fraction (B) melting at about 205–10° could be obtained after repeated crystallisations using ethyl acetate, besides fractions melting at 210–22°, a definite compound (M) melting at 235–36°. Further crystallisation of this compound from the same solvent raised the melting point to 239–40°. It has the formula $C_{32}H_{52}O_2$ and it is found to be an ester yielding on saponification acetic acid and a triterpene alcohol which has been identified as β-amyrin from a detailed study of its properties and the preparation of its derivatives. It therefore follows that the original substance (M) is β-amyrin acetate. Fractions melting between 210–22° could not be further purified but they had the same composition as (M). They were obviously mixtures of β-amyrin acetate with compounds of the same type which are isomeric with it.

The resinols were found to be present to a minor extent in the waxy portion and to a much higher degree in fraction (A) of the alcohol-soluble portion. The preliminary saponification and careful separation into various fractions of the unsaponifiable matter rendered identification of various components easy. By this means the sterols were effectively removed from

the resinols. The separation and identification of the resinol mixtures have been carried out by the acetate as well as by the benzoate methods. Fraction I melting at 175–85° has been found to consist mostly of α-amyrin admixed with small amounts of β-amyrin. The second fraction melting at 160–65° contained lupeol as the main component and it was best isolated as the benzoate. The amyrins were present only in small quantities.

Fractions III, IV, V and VI melting at 155–57° and below were individually examined. Fraction III melting at 155–57° contained β-amyrin and lupeol and very little of α-amyrin. The other lower fractions (IV, V and VI) were very similar to it having the three above compounds in varying proportions. Further in all of them were present small quantities of substances whose acetates were markedly more soluble in alcohol than those of the above resinols and which differed from them in giving a display of colours (pink-blue-green) with the Liebermann-Burchard reagent though they gave the same yellow colour with green fluoresence with the Salkowski's reagent. Thus they exhibited characteristics, partly of sterols and partly of resinols. They are being further investigated.

Hemidesmus indicus.—It was pointed out in Part III[2] that the composition of the petroleum ether extract of this root agrees closely with that of the *Decalepis* and that what Dutta, Ghosh and Chopra considered to be new sterols were really mixtures of resinols with small quantities of sterols. This is now definitely supported by careful examination of the various resinol fractions. The presence of lupeol and of α- and β-amyrins has been established. The compound melting at 235–36° has been identified as β-amyrin-acetate. During the careful examination of the various fractions, the special type of compounds mentioned in the case of the *Decalepis* as giving display of colours with the Liebermann-Burchard reagent and only yellow colour with Salkowski's reagent was also met with here. Besides these a small quantity of a substance which is characterised by the yellow coloured solution having a brilliant green fluorescence which it gives with the Liebermann-Burchard reagent is obtained. With the Salkowski's reagent it gives only an yellow colour. This probably belongs to the tetracyclic triterpene type and this surmise gains support from the fact that on boiling with formic acid and benzene it undergoes transformation into a product of the pentacyclic type whose formation was indicated by the typical resinol colour reactions. The yield however was very small and a detailed study could not be carried out so far.

The results so far obtained may be summed up as follows : Though the two roots contained the same resinols the *Decalepis* has in it more of

amyrins than lupeol whereas in the case of the *Hemidesmus* roots the position is just the reverse.

Experimental

Decalepis Hamiltonii: *Identification of β-amyrin acetate.*—The crystalline compound (M) melting at 235–36° (0·5 g.) was heated under reflux with 6% alcoholic potash (25 c.c.) for 5 hours and the contents were largely diluted with water. The crystalline precipitate that was formed was filtered and recrystallised from alcohol when it was obtained as needles melting at 196–97°. [Found: C, 83·8; H, 11·2; $C_{30}H_{50}O$ requires C, 84·4; H, 11·7%.] This was identified as β-amyrin by comparison with a sample described later on; the mixed melting point was undepressed. The filtrate was concentrated to a small bulk, acidified with dilute sulphuric acid and steam-distilled. In the distillate the presence of acetic acid was established by performing the lanthanum nitrate test carried out according to the procedure of Neelakantam and Row.[3] Hence the original compound (M) was identified as β-amyrin acetate. The melting point rose to 239–40° after further crystallisation and it was unaffected by admixture with a sample of β-amyrin acetate whose detailed study is given later on in this paper. The results of combustion analysis have been given in Part I and they agree with the formula $C_{32}H_{52}O_2$.

As already described in Part I the resinols from (A) were fractionated into six fractions and the corresponding fractions from (W) were added to them ; fraction I had m.p. 175–85°; II, 160–65°; III, 155–57°; IV, 151–53°; V, 135–45° and fraction VI, 130–35°.

Resinol fraction I (*m.p.* 175–85°): *Separation by the acetate method.*—The solid (2 g.) was boiled with acetic anhydride (10 c.c.) and sodium acetate (4 g.) for 2½ hours and the mixture poured into water. After allowing it to stand for 12 hours the solid product was separated and crystallised from alcohol whereby a crop of crystals melting at 215° were obtained. Further repeated crystallisation from ethyl acetate raised the melting point to 222–23° and at this stage the solid appeared as colourless shining elongated plates. [Found: C, 81·6; H, 10·9; $C_{32}H_{52}O_2$ requires C, 82·1; H, 11·1%.] $[\alpha]_D^{28}$, + 81·5° in chloroform and that already recorded for α-amyrin acetate is + 83·0°.

The acetate was hydrolysed by heating with 5% alcoholic potash for 3 hours. After dilution with excess of water the resulting solid was crystallised from alcohol when glistening colourless needles melting at 185–87° were obtained. [Found: C, 84·0; H, 11·6; $C_{30}H_{50}O$ requires C, 84·4; H, 11·7%.] $[\alpha]_D^{28}$ in benzene, +92·1° and the value noted by previous workers for α-amyrin + 93·3°. Thus the presence of α-amyrin in this fraction was established. This was further confirmed by the preparation of the benzoate

which melted at 192° (described later). The mother-liquor and washings from the crystallisation of the above-mentioned acetate were mixed and the solvent removed. The solid residue thus obtained melted at 160–70°. It was first boiled with a small amount of methyl alcohol and filtered and subsequently recrystallised from ethyl acetate. It now melted at 215–18° and it could not be further purified by the ordinary methods. [Found: C, 81·9; H, 11·9; $C_{32}H_{52}O$ requires C, 82·1; H, 11·1%.] On hydrolysis and purification of the resulting alcohol could be obtained a small quantity of β-amyrin melting at 196–97° and a larger quantity of α-amyrin melting at 185–87°.

Separation by benzoate method.—The crystalline solid (2 g.) was dissolved in dry benzene (20 c.c.) and treated in the cold with benzoyl chloride (10 c.c.) and pyridine (7 c.c.). The mixture was allowed to stand overnight and finally heated under reflux for 2 hours. The contents were then diluted with water and extracted with excess of benzene. The benzene solution was evaporated to dryness, the residue taken up in ether and shaken successively with aqueous sodium hydroxide, aqueous sulphuric acid and water. On concentrating the ether solution and cooling in ice colourless needles of a solid melting at about 190° were obtained. When further recrystallised from ligroin and benzene-alcohol mixture, the substance finally melted at 192–93°. [Found: C, 83·6; H, 10·2; and $C_{37}H_{54}O_2$ requires C, 83·8; H, 10·2%.] $[\alpha]_D^{28}$ in benzene, + 90·0° and that recorded by previous workers for α-amyrin benzoate in benzene solution is + 87·3°. Further crops of the same substance could be obtained on concentrating the ether solution and recrystallising the solid from benzene-alcohol mixture. The final fractions, however, melted at 165–75° and no pure compound could be obtained from them. The benzoate was hydrolysed by heating with 5% alcoholic potash for 5 hours. By diluting the contents with a large excess of water and crystallising the resulting solid from alcohol, shining colourless needles melting at 185–87° were obtained and these were found to be identical with the sample of α-amyrin obtained from the acetate method.

From the results of analysis of the free alcohol, its acetate and benzoate and from their properties particularly specific rotations the presence of α-amyrin in fraction (I) as the predominant component is established. β-Amyrin is present only in minor quantities.

Fraction II (*m.p.* 160–65°).—This solid (5·0 g.) was dissolved in benzene (25 c.c.) and benzoyl chloride (15 c.c.) and pyridine (10 c.c.) added. The benzoylation was effected just as before. The crude benzoate mixture melted at 180° and when this was boiled with a small amount of methyl alcohol and filtered, the melting point rose to 210–20°. Subsequent crystallisation

from ether yielded a compound melting at 249–54°. Final recrystallisation (3 times) from ligroin yielded colourless gritty broad rectangular plates melting at 261–62°. No change was effected by further crystallisation. [Found: C, 83·4; H, 10·5; $C_{37}H_{54}O_2$ requires C, 83·8; H, 10·2%.] $[\alpha]_D^{28}$, + 62·5° in chloroform solution and $[\alpha]_D$ noted in the literature for lupeol benzoate, + 60·9°.

The benzoate was hydrolysed by heating with alcoholic potash for 5 hours according to the procedure already described. The product was subjected to slow crystallisation from a mixture of alcohol and acetone. By this means long needles, melting at 211–12°, were obtained. Further crystallisation did not bring about any change. [Found: C, 84·0; H, 11·1; $C_{30}H_{50}O$ requires C, 84·4; H, 11·7%.] $[\alpha]_D^{28}$ in chloroform, + 41·0° and that recorded for lupeol, + 41·2°. From all the above results it is concluded that lupeol is present in this fraction.

The mother-liquor and washings from lupeol benzoate were mixed and concentrated. First crops of crystals melting at 240–50° were obtained which eventually yielded on purification lupeol benzoate. Subsequent crops yielded on recrystallisation (4 times) from benzene-alcohol mixture a small quantity (0·2 g.) of a solid melting at 231–32°. [Found: C, 84·2; H, 10·4; and $C_{37}H_{54}O_2$ requires C, 83·8; H, 10·2%.] This benzoate on hydrolysis with alcoholic potash yielded a compound melting at 197–98° which was found to be identical with β-amyrin obtained from the acetate melting at 239°. The mixed melting point was not lowered. Hence the presence of a small quantity of β-amyrin in this fraction was established.

The final mother from the above benzoates was evaporated to dryness and the residue dissolved in benzene-alcohol mixture and allowed to crystallise slowly. After removing some indefinitely melting fractions α-amyrin benzoate melting at 192–93°, was obtained in well-defined needles and was found to be identical with the sample of the benzoate obtained from the first fraction. The final residues yielded a solid melting at 140–70°.

Hence fraction (II) contains lupeol as the main component mixed with α- and β-amyrins, the last being in the smallest quantity.

Fractions III, IV, V and VI.—(Resinols melting between 130–57°.) All these fractions gave very similar results. They were first acetylated and the acetates fractionally crystallised from alcohol. A very small quantity of sparingly soluble fraction (1) melting at 235° was obtained. After further crystallisation from ethyl acetate it was found to be β-amyrin acetate. Subsequently several fractions (2) were collected from the alcohol solution. One of these melted fairly sharp at 165–66° and on analysis yielded the following

results. [Found: C, 82·3; H, 10·6; and $C_{32}H_{52}O_2$ requires C, 82·1; H, 11·1%.]

All these gave the pink colour with Liebermann-Burchard reagent and yellow colour with green fluorescence with Salkowski's reagent. The last and the most soluble fraction melted indefinitely at 120° and exhibited certain peculiar colour reactions. With the Liebermann-Burchard reagent it gave a play of colours pink-blue-green and with the Salkowski's reagent the sulphuric acid layer assumed orange yellow with green fluorescence on standing. These characteristics differ from those of well-known sterols and resinols and hence this fraction is being further examined.

The middle fraction of the acetates (2) given above could not be further satisfactorily separated into definite compounds. It was therefore hydrolysed and the free alcohols benzoylated. From this product, benzoates of lupeol, β-amyrin and α-amyrin could be obtained. Lupeol seemed to be the most important component in these fractions also.

Hemidesmus indicus.—Fractions I (m.p. 175–85°), II (m.p. 165–70°), III (m.p. 155–65°) and IV (m.p. 150–54°) gave very similar results, hence they are reported together. First they were acetylated and the acetates fractionally crystallised from alcohol. The more sparingly soluble portion (A) melting at 190–200° was repeatedly recrystallised from ethyl acetate when a very small quantity of β-amyrin acetate melting at 236° separated first. Subsequently the bulk of the acetate portion separated out melting at about 200°. After repeated recrystallisation (6 times) from ethyl acetate pure lupeol acetate (shining flat needles) melting at 214° was obtained from it. [Found: C, 81·8; H, 10·4; $C_{32}H_{52}O_2$ requires C, 82·1; H, 11·1%.] $[\alpha]_D^{28}$, + 45·4° in chloroform solution and $[\alpha]_D$ for lupeol acetate is given in the literature as + 47·1° in chloroform. The melting point was not depressed when mixed with lupeol acetate from *D. Hamiltonii*. When hydrolysed with alcoholic potash the acetate yielded a product which could be easily crystallised from alcohol. It was obtained as silky needles melting at 212° (Lupeol). $[\alpha]_D$ in chloroform solution is + 41·1° and that recorded for lupeol is + 41·2°. Further no depression in the melting point was observed when mixed with the lupeol obtained from the *Decalepis* roots.

The alcohol mother-liquor from the crystallisation of acetates gave indefinite mixtures melting at 165–95° and they were not further examined.

Fractions I and II were also benzoylated and the mixture of benzoates examined as in the case of *Decalepis Hamiltonii*. Pure lupeol benzoate was easily obtained from ligroin in a good yield from the first crop of crystals and the mother-liquor yielded indefinite mixtures melting at 180–220°. It was

therefore concluded that lupeol was the main component of these fractions and the amyrins probably occurred along with it. The presence of β-amyrin was definitely established.

Fraction V (*m.p.* 135–40°).—This fraction was acetylated and the acetates were subjected to careful fractionation from an alcohol solution. It was noticed that the first fractions (m.p. 185–200°) gave the usual tests for the pentacyclic resinols, *i.e.*, a pink colour with the Liebermann-Burchard reagent and a yellow solution with the Salkowski's reagent. From the middle portions could be obtained a small quantity of a colourless solid melting at 135–45°. This behaved differently. With the Liebermann-Burchard reagent it gave a yellow solution with brilliant green fluorescence and the solution slowly assumed faint pink colour on standing. No test was given with Salkowski's reagent, only a very pale yellow soluion being produced. This has been noted as the characteristic colour reaction of tetracyclic triterpenes and hence a sample of the substance was heated under reflux with a mixture of formic acid and benzene for 2 hours in order to bring about the formation of the pentacyclic triterpenes. After crystallisation from ethyl acetate the product melted at about 195° and it produced the usual pink colour with the Liebermann-Burchard reagent. Hence the existence of the tetracyclic compounds in the fraction V was indicated.

The final fractions of the acetates gave with the Liebernmann-Burchard reagent a play of colours pink-blue-green but produced no red colour with Salkowski's reagent. These seem to be the same as the substances obtained in a similar manner from *Decalepis Hamiltonii*. The quantity was however too small to permit detailed study.

Summary

The existence of resinol in the petrol-soluble portions of *Decalepis Hamiltonii* and *Hemidesmus indicus* has been established by the isolation of α- and β-amyrins and lupeol from them. They exist both free and as esters. The various fractions have been analysed using both the acetate and the benzoate methods. The roots of the *Decalepis* contain more of the amyrins and less of lupeol whereas the *Hemidesmus* contains more of lupeol. The more soluble fractions of both roots seem to possess certain compounds having partly the properties of sterols and partly those of resinols. Further in *Hemidesmus* roots small amounts of tetracyclic triterpene alcohols also seem to be present.

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2. ———————— .. *Ibid.*, **13**, No. 5, 399.
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HETEROCYCLIC COMPOUNDS

Part XIV. Coumarins from 4-Ethyl-2-acetylresorcinol and β-Ketonic Esters

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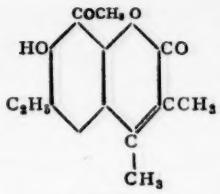
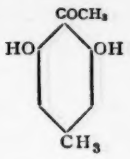
It has been shown by Desai and co-workers[1] that resacetophenone as well as 5-ethyl-2 : 4-dihydroxy-acetophenone condense with aceto-acetic ester, not in the presence of concentrated sulphuric acid, but phosphoryl chloride with the formation of 7-hydroxy-coumarin derivatives. Limaye and Shenolikar,[2] on the other hand, have found that 2-acetylresorcinol undergoes the usual coumarin condensation in the presence of concentrated sulphuric acid. Desai and Ekhlas[3] who happened to synthesise 4-ethyl-2-acetylresorcinol in course of some other work observed that it resembled 2-acetylresorcinol in its capacity for coumarin condensation in the presence of concentrated sulphuric acid. To make sure that this was not an isolated case, we have now condensed 4-ethyl-2-acetylresorcinol with C-alkylated aceto-acetic esters of the general formula CH_3–CO–CHR COOEt, where R = methyl, ethyl, propyl, butyl and allyl groups. Thus methylaceto-acetic ester gave 3 : 4-dimethyl-6-ethyl-7-hydroxy-8-acetyl coumarin (I) while its higher homologues behaved in an analogous manner.

The constitution of the resulting coumarin was proved by its rational synthesis from 4-ethylresorcinol and methylaceto-acetic ester which gave 3 : 4-dimethyl-6-ethyl-7-hydroxycoumarin, the acetoxy derivative of which underwent Fries migration with the formation of 3 : 4-dimethyl-6-ethyl-7-hydroxy-8-acetylcoumarin. The constitution of other coumarins was similarly proved, and this proof is conclusive as Desai and Ekhlas[1] have shown that the Pechmann condensation of 4-ethylresorcinol and aceto-acetic ester gives exclusively 6-ethyl-7-hydroxy-4-methylcoumarin.

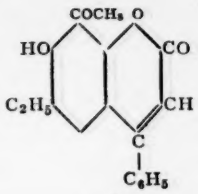
Desai and Miss Vakil[4] have recently shown that 5-methyl-2-acetylresorcinol (II) undergoes de-acetylation during the course of the Pechmann Reaction. When this observation is compared with those recorded in this communication it becomes quite apparent how profoundly similar substituents situated in different places affect the course of the same reaction.



(I)



(II)



(III)

Finally 4-ethyl-2-acetylresorcinol was condensed with benzoyl acetic ester, when 4-phenyl-6-ethyl-7-hydroxy-8-acetylcoumarin (III) was obtained. The poor yield obtained in this reaction shows that this ester is less reactive than aceto-acetic ester.

Experimental

4-Ethyl-2-acetylresorcinol was prepared by Limaye's Process the details of which have been described by Desai and Ekhlas[3] (*loc. cit.*). These have been recently repeated and confirmed by Limaye and Limaye.[5]

Condensation of 4-ethyl-2-acetylresorcinol with ethyl α-methylaceto-acetate and formation of 3 : 4-dimethyl-6-ethyl-7-hydroxy-8-acetyl-coumarin.—A clear solution of the dihydroxy ketone (2·5 g.) and the ester (2 g.) in 73 per cent. sulphuric acid (25 c.c.) was kept at the room temperature for 36 hours, and poured over ice. The resulting solid crystallised from alcohol in colourless needles, m.p. 121° (yield = 75 per cent.).

[Found: C, 69·1; H, 6·2; $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2 per cent.]

The coumarin was easily soluble in chloroform, acetone, alcohol and acetic acid, sparingly soluble in benzene but almost insoluble in petroleum ether. Its alkaline solution was yellow and devoid of any fluorescence, and its alcoholic solution gave green colouration with alcoholic ferric chloride.

Condensation of 4-ethylresorcinol with ethyl α-methylaceto-acetate and formation of 3 : 4-dimethyl-6-ethyl-7-hydroxycoumarin.—A mixture of 4-ethylresorcinol (3 g.), α-methylaceto-acetic ester (3 g.) and 73 per cent. sulphuric acid (30 c.c.), after being kept for 12 hours was poured over rice. The solid crystallised from alcohol in colourless needles, m.p. 240° (yield = 90 per cent.).

[Found: C, 71·4; H, 6·55; $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·5 per cent.]

It dissolved in alkali giving green fluorescence. The *acetyl* derivative prepared by heating the mixture of the coumarin (2 g.), acetic anhydride (10 c.c.) and fused sodium acetate (2 g.) for four hours crystallised from alcohol in lustrous needles, m.p. 150°.

[Found: C, 69·0; H, 6·3; $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2 per cent.]

Fries Transformation of 3: 4-*dimethyl*-6-*ethyl*-7-*acetoxy-coumarin to* 3: 4-*dimethyl*-6-*ethyl*-7-*hydroxy*-8-*acetylcoumarin.*—An intimate mixture of the acetoxy coumarin (1 g.) and anhydrous aluminium chloride (2 g.) was gradually heated in an oil-bath to 140° for one hour. The solid obtained by decomposing the excess of aluminium chloride with ice-cold hydrochloric acid was purified through alkali, and crystallised from alcohol when colourless needles, m.p. 121°, were obtained. Its m.p. was not depressed by the specimen prepared from 4-ethyl-2-acetylresorcinol and α-methylaceto-acetate.

Condensation of α-*ethylaceto-acetate with* 4-*ethyl*-2-*acetylresorcinol and formation of* 3: 6-*diethyl*-4-*methyl*-7-*hydroxy*-8-*acetylcoumarin.*—This was carried out as above. The *Coumarin* which was obtained in 70 per cent. yield crystallised from alcohol in colourless needles, m.p. 147°. Its alkaline solution was yellow and non-fluorescent, while its alcoholic solution gave green colouration with alcoholic ferric chloride.

[Found: C, 69·8; H, 6·8; $C_{16}H_{18}O_4$ requires C, 70·0; H, 6·8 per cent.]

3: 6-*Diethyl*-4-*methyl*-7-*hydroxycoumarin* was obtained by the usual method by condensing 4-ethylresorcinol with α-ethylaceto-acetic ester, and crystallised from alcohol in needles, m.p. 216°.; (yield = 75 per cent.). Its alkaline solution was yellowish and gave green fluorescence.

[Found: C, 72·2; H, 7·0; $C_{14}H_{16}O_3$ requires C, 72·4; H, 7·1 per cent.]

The Acetyl Derivative crystallised from alcohol in lustrous needles, m.p. 131°.

[Found: C, 70·1; H, 6·8; $C_{16}H_{18}O_4$ requires C, 70·0; H, 6·6 per cent.]

When subjected to the Fries Transformation in the usual manner, the above acetyl-derivative gave 3: 6-diethyl-4-methyl-7-hydroxy-8-acetyl-coumarin, m.p. 147°, and undepressed by the sample prepared from 4-ethyl-2-acetyl-resorcinol and α-ethylaceto-acetic ester.

Condensation of α-*propyl-acetoacetate with* 4-*ethyl*-2-*acetylresorcinol and formation of* 3-*propyl*-4-*methyl*-6-*ethyl*-7-*hydroxy*-8-*acetylcoumarin.*—This coumarin (70 per cent. yield) crystallised from alcohol in colourless needles, m.p. 129°, and had the usual properties of its analogues.

[Found: C, 70·6; H, 7·2; $C_{17}H_{20}O_4$ requires C, 70·8; H, 7·0 per cent.]

3-*Propyl*-4-*methyl*-6-*ethyl*-7-*hydroxy-coumarin* obtained from 4-ethyl-resorcinol and α-propylaceto-acetic ester (65 per cent. yield) crystallised from alcohol in yellowish needles, m.p. 189°.

[Found: C, 72·9; H, 7·5; $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4 per cent.]

The Acetyl Derivative crystallised from alcohol in needles, m.p. 133.°

[Found: C, 70·6; H, 7·2; $C_{17}H_{20}O_4$ requires C, 70·9; H, 7·3 per cent.]

When this was subjected to the Fries migration it gave the coumarin m.p. 129°, which was proved to be 3-propyl-4-methyl-6-ethyl-7-hydroxy-8-acetylcoumarin.

Condensation of 4-*ethyl*-2-*acetylresorcinol with* α-*butylacetoacetate and formation of* 3-*butyl*-4-*methyl*-6-*ethyl*-7-*hydroxy*-8-*acetylcoumarin.*—As the α-butylaceto-acetic ester was slightly contaminated with the original unsubstituted aceto-acetic ester, the crude coumarin was fractionally crystallised from alcohol. The first fraction, m.p. 135°, was identified as 4-methyl-6-ethyl-7-hydroxy-8-acetylcoumarin while the second fraction, m.p. 100-105°, when recrystallised from benzene, melted at 124°. Its alcoholic solution gave green colouration with ferric chloride, and was identified to be 3-*Butyl*-4-*methyl*-6-*ethyl*-7-*hydroxy*-8-*acetylcoumarin.*

[Found: C, 71·2; H, 7·5; $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·3 per cent.]

The coumarin obtained by condensing 4-ethylresorcinol with α-butyl-acetoacetic ester was a mixture of 3-*butyl*-4-*methyl*-6-*ethyl*-7-*hydroxycoumarin* and 4-methyl-6-ethyl-7-hydroxycoumarin. The former was more soluble in warm benzene than the latter. The soluble fraction on recrystallisation from alcohol gave colourless needles, m.p. 159°.

[Found: C, 73·5; H, 7·9; $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·8 per cent.]

The Acetyl Derivative crystallised from alcohol in lustrous needles, m.p. 114°.

[Found: C, 71·3; H, 7·5; $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·3 per cent.]

When subjected to the Fries Transformation, it gave a product, m.p. 124°, identified by the mixed m.p. as 3-butyl-4-methyl-6-ethyl-7-hydroxy-8-acetyl-coumarin which has been described before.

Condensation of α-*allyl-aceto-acetic ester with* 4-*ethyl*-2-*acetylresorcinol and formation of* 3-*allyl*-4-*methyl*-6-*ethyl*-7-*hydroxy*-8-*acetylcoumarin.*—This coumarin crystallised from alcohol in yellowish needles, m.p. 106° (yield = 50 per cent.).

[Found: C, 71·0; H, 6·5; $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·4 per cent.]

4-*Ethylresorcinol* condensed with α-allyl-aceto-acetic ester in the usual manner giving 3-*allyl*-4-*methyl*-6-*ethyl*-7-*hydroxycoumarin* which crystallised from alcohol in needles, m.p. 202° (yield = 45 per cent.).

[Found: C, 73·5; H, 6·4; $C_{15}H_{16}O_3$ requires C, 73·7; H, 6·6 per cent.]

The Acetyl Derivative crystallised from alcohol in needles, m.p. 123°.

[Found: C, 71·1; H, 6·6; $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3 per cent.]

The Fries migration of this acetyl derivative gave the coumarin, m.p. 106° and identified as 3-*allyl*-4-*methyl*-6-*ethyl*-7-*hydroxy*-8-*acetylcoumarin*.

Condensation of benzoylacetic ester with 4-*ethyl*-2-*acetylresorcinol and ormation of* 4-*phenyl*-6-*ethyl*-7-*hydroxy*-8-*acetylcoumarin*.—The condensation carried out as usual was worked up after 36 hours when the resulting coumarin crystallised from alcohol in lustrous, prismatic needles, m.p. 154° (yield = 180 per cent.). Its alkaline solution was yellow and non-fluorescent while the alcoholic solution gave deep-violet colouration with alcoholic ferric chloride.

[Found: C, 73·8; H, 5·4; $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2 per cent.]

4-*Phenyl*-6-*ethyl*-7-*hydroxycoumarin*, obtained from 4-ethylresorcinol and benzoylacetic ester, crystallised from alcohol in colourless lustrous needles, m.p. 232° (yield = 90 per cent.). Its yellowish, alkaline solution gave green fluorescence.

[Found: C, 76·5; H, 5·5; $C_{17}H_{14}O_3$ requires C, 76·6; H, 5·3 per cent.]

The Acetyl Derivative crystallised from alcohol in lustrous needles, m.p. 151°.

[Found: C, 73·7; H, 5·4; $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2 per cent.]

When this acetyl derivative was subjected to the usual Fries migration, 4-*phenyl*-6-*ethyl*-7-*hydroxy*-8-*acetylcoumarin*, m.p. 154°, was obtained.

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Summary

The condensation of 4-ethyl-2-acetylresorcinol with α-methyl, α-ethyl, α-propyl, α-butyl and α-allylaceto-acetic esters as well as benzoylacetic ester has shown that this ketone is much reactive as contrasted with resacetophenone, thus showing that the Pechmann Reaction is not hindered by negative groups in the γ-position of the resorcinol molecule. The constitution of each coumarin was established by its rational synthesis from 4-ethylresorcinol, acetylating the resulting coumarin, and subjecting it to the Fries migration.

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COLOURING MATTER OF THE FLOWERS OF *HIBISCUS CANNABINUS* : CONSTITUTION OF CANNABISCETIN

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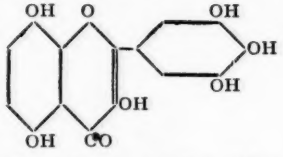
Hibiscus cannabinus (Deccan Hemp) is a small shrub cultivated in India for the sake of its valuable fibre and also as a vegetable. The flowers are light yellow in colour with a purple centre. A preliminary report of the chemical investigation of these flowers was made sometime back by Neelakantam and Seshadri[1] who announced the isolation of a new flavonol and its glucoside. They were named Cannabiscetin and Cannabiscitrin respectively because of their first isolation from the flowers of the cannabinus. Subsequently results have been obtained giving information regarding the constitution of the aglucone. A detailed account of the preparation and properties of the pigments and the determination of the constitution of cannabiscetin is given in this paper.

The dried petals were extracted with methylated spirit and the pigments isolated in various fractions according to the procedure already outlined in connection with other flowers.[2] The first fraction which was sparingly soluble in alcohol and came out on concentrating the alcoholic extract, consisted of the glucoside, cannabiscitrin. The aqueous solution subsequently obtained by diluting the alcoholic mother-liquor and removing the alcohol did not deposit any solid, but, when extracted with ether, yielded the aglucone, cannabiscetin. The neutral lead acetate fraction also seemed to consist mostly of the glucoside, which was, however, difficult to be purified. But pure cannabiscetin could be readily obtained therefrom after hydrolysis. The basic lead acetate fraction was too small to be studied. It could, therefore, be concluded that the colouring matter consists mostly of cannabiscitrin along with small quantities of the aglucone.

Cannabiscitrin has the formula $C_{21}H_{20}O_{13}$ and decomposes at about 245°. With alkaline buffer solutions, the substance yields two characteristic colorations—green and orange, the yellow colour that is first produced being evanescent. On acetylation it produces a colourless nonaacetyl derivative, and on hydrolysis with dilute sulphuric acid, it gives rise to glucose and the aglucone, cannabiscetin.

Cannabiscetin has the formula $C_{15}H_{10}O_8$ and does not melt below 350°. With ferric chloride, it gives a brown-black colour, and with dilute alkali, it undergoes a series of colour changes—yellow, green, blue, then olive green and finally light-brown. With alkaline buffer solutions the characteristic colorations are green, blue, crimson and purple, the initial yellow changing almost instantaneously, and these colour changes enable the flavonol to be easily distinguished from its glucoside. It yields a hexaacetyl derivative and a hexamethyl ether, thereby indicating the presence of six hydroxyl groups. It gives a deep red precipitate with neutral lead acetate solution, and undergoes decomposition with alkali and air; hence it should be a flavonol. It is isomeric with gossypetin, myricetin and quercetagetin. When treated with *p*-benzoquinone, it gives the " gossypetone " reaction just like gossypetin or herbacetin, thereby showing the presence of two hydroxyl groups in 5 and 8 positions. This is further supported by the rapid colour changes in alkaline buffer solutions just as in the case of gossypetin and herbacetin. As the result of oxidation in an alkaline solution exposed to air, it produces gallic acid which could be isolated and identified as its trimethyl ether. The completely methylated ether also yields trimethyl gallic acid, when boiled with 50% potash. These experiments prove the existence of hydroxyl groups in 3′, 4′ and 5′ positions. Hence cannabiscetin may be represented as 3 : 5 : 8 : 3′ : 4′ : 5′-hexahydroxy flavone.



Further details regarding the properties of cannabiscitrin and the position of the sugar group will be published later.

Experimental

Fraction 1—

Isolation of Cannabiscitrin.—Dry petals of the flowers of *Hibiscus cannabinus* (2 kg.) were extracted twice with methylated spirit, each extraction lasting for about 12 hours. The total alcoholic extract was concentrated to about 500 c.c. On leaving overnight a good amount of resin and wax separated out from the concentrate. They were removed by filtration through fluted filters. When the clear filtrate was allowed to stand for about 10 days, it deposited a large quantity of a yellow crystalline solid. It was filtered, and washed well with water till it assumed a pale yellow colour. It was then dissolved in pyridine and the solution diluted with water till the

impurities just began to separate out in a colloidal form. They were precipitated by adding a few drops of calcium chloride solution and then filtered. The clear filtrate which did not separate out any more impurities on further dilution, was concentrated on a water-bath till solid began to appear on the surface of the liquid. On leaving overnight, a good amount of a deep yellow crystalline substance separated. It was recrystallised from dilute pyridine, when it came down as rods and plates (25 g.). It crystallised from dilute acetic acid as clusters of short yellow needles. On heating, it sintered at 210° fused at 220°, and decomposed at 245°. [Found in air-dried sample: C, 46·7; H, 5·1; and loss on drying 10·0; $C_{21}H_{20}O_{13}$, 3 H_2O requires C, 47·2; H, 4·9; and loss (H_2O) on drying 10·1%. [Found in the sample dried *in vacuo* at 110°: C, 51·9 ; H, 4·3 ; $C_{21}H_{20}O_{13}$ requires C, 52·5; H, 4·2%.]

The glucoside was found to be easily soluble in alcohol, dilute and glacial acetic acids, and pyridine. When an aqueous alcoholic solution of the substance was treated with a drop of alkali, an olive-green colour was obtained; on adding more alkali, a pure yellow solution was produced. An alcoholic solution gave a reddish orange precipitate with neutral lead acetate, and with ferric chloride an olive-green colour which faded rapidly to dark-brown.

On boiling with acetic anhydride and anhydrous sodium acetate, the pigment yielded the nonaacetate. It crystallised from glacial acetic acid (animal charcoal) as fine colourless needles. It was sparingly soluble in alcohol and even dilute acetic acid. A mixture of acetic anhydride and alcohol was found to be a convenient solvent for crystallisation. On heating it melted into a glassy mass at 200–02° and did not flow down even at 260°. [Found: C, 54·3; H, 4·4; $C_{21}H_{11}O_4(OCOCH_3)_9$ requires C, 54·5; H, 4·4%.]

Hydrolysis of the Glucoside : *Preparation of Cannabiscetin.*—The glucoside (2 g.) was hydrolysed by boiling with 7% sulphuric acid (50 c.c.). The solid went into solution on boiling for some time and within half an hour, the aglucone separated out giving rise to bumping. However the boiling was continued carefully over a mild flame for two hours. After cooling, the solid was filtered and crystallised from glacial acetic acid. It did not melt below 350°. When allowed to crystallise slowly, it came out as large yellow rectangular plates and prisms, but on rapid crystallisation it was obtained as flat needles and narrow plates. The yield was 1·2 g. [Found in air-dried specimen : C, 53·7; H, 3·8; loss on drying 5·2%; $C_{15}H_{10}O_8$, H_2O requires C, 53·6; H, 3·6 and loss on drying (H_2O) 5·4%. Found in the sample dried at 110°: C, 56·4; H, 3·5; $C_{15}H_{10}O_8$ requires C, 56·6, H 3·1%.]

From the acid filtrate left after the removal of the aglucone, glucose was isolated in the form of its osazone by neutralising it with barium carbonate, concentrating it on a water-bath and subsequently treating it with phenyl hydrazine.

Fraction II—

Cannabiscetin.—The alcoholic mother-liquor remaining after the separation of the glucoside was concentrated to half its bulk and cooled. As no precipitate was thereby obtained, the solution was considerably diluted with water and the alcohol was removed almost completely on a water-bath. The resin that separated out during the course of this operation was carefully removed by decanting the liquid into a fluted filter. The clear filtrate was further concentrated and cooled. As no precipitate was obtained from this liquor even after several days, it was repeatedly extracted with ether. On distilling off the ether, a yellow crystalline solid was obtained (1 g.). It was purified by crystallisation from dilute alcohol, when it appeared in the form of plates and prisms. The substance did not melt below 350°. It was identical in all its properties with cannabiscetin obtained from the new glucoside as already described. The identity was confirmed by preparing their acetyl derivatives and taking their mixed melting point.

Neutral Lead Acetate Fraction.—The aqueous solution left after extraction with ether, did not deposit any solid on standing even for 15 days. It was then treated with neutral lead acetate solution, when an orange-red precipitate was obtained. From this lead salt the pigment was liberated by passing hydrogen sulphide repeatedly into its suspension in water. The precipitated lead sulphide was filtered off and the filtrate concentrated on a water-bath. But no solid separated out even after several days. Hence the calculated amount of concentrated sulphuric acid was added to make the solution 7% in the acid content and then boiled for two hours in order to hydrolyse any glucosides that might have been present. By this treatment a yellow crystalline substance was obtained (1 g.). It was identified as cannabiscetin by comparison of the pigment and its acetyl derivative with authentic samples.

Properties of Cannabiscetin.—The pigment was sparingly soluble in alcohol but it freely dissolved in glacial acetic acid and pyridine. It produced a deep red precipitate with lead acetate and a dark-brown colour with ferric chloride. It dissolved in very dilute alkali, producing at first a yellow solution which rapidly changed to green and then blue, gradually to olive-green and finally to light-brown.

Colour Reactions of the Aglucone and its Glucoside with Alkaline Buffer Solutions.—Both the aglucone and the glucoside showed prominent colour

changes with alkaline buffer solutions of only high pH value; the following table summarises the changes :

pH	Aglucone	Glucoside
8·0	Slowly dissolved to form a pale yellow solution which changed to yellowish brown after 24 hours.	Dissolved slowly to a pale yellow solution which became yellowish red after 24 hours.
8·6	The dissolution was more quick and the yellow solution acquired an orange tinge within an hour and became yellowish brown after 24 hours.	Same changes as above but more rapid.
9·2	Quickly dissolved, yielding a yellow solution, with a green tinge. The colour rapidly changed to yellowish green, then yellowish brown and to pure brown within 10 minutes. The brown became orange-red which was stable for an hour. The next day, it was still brown.	Same changes as above; but the final colour was orange-yellow (after 24 hours).
9·8	The initial yellow solution quickly turned to green and became within 5 minutes brown through dirty brown. It became orange-red within 10 minutes and remained so for an hour. After 24 hours it was brown.	Dissolved very quickly to produce a clear yellow solution which became orange after 24 hours.
10·4	Quick succession of changes :—yellow solution—bright emerald green—greenish-brown—brown—reddish brown —bright crimson (within 5 minutes). The crimson colour was stable for 1 hour and faded to brown the next day.	Quick succession of changes :—yellow solution —yellowish green—again yellow. The solution slowly acquired an orange tinge and after 24 hours became definitely orange with a strong green fluorescence.
11·0	Same changes as above but more quick, the crimson appearing even within 2 minutes. Subsequent behaviour was also just the same.	Rapid changes :—Yellow solution—greenish yellow—orange. It became brown after 24 hours.
11·6	The yellow solution changed rapidly to purple which gradually became reddish purple within an hour. It became brown as usual after 24 hours.	The yellow solution rapidly changed to green and became almost colourless within 10 minutes. After 24 hours it was brown.
12·2	Same changes as above ; but the initial purple was mixed up with violet.	Same changes as above.
12·8	Very quick changes :—yellow solution —emerald green—deep pure blue—purple—brown (within 5 minutes). The last colour faded quickly to pale yellowish-brown which was stable for 1 hour, and became dirty brown after 24 hours.	Same changes as above ; but the tinge after 24 hours was green-brown.
13·4	Same changes as above ; but the purple was less prominent.	Same changes as above, the green-brown giving place to faint brown.

Preparation of Hexaacetyl Cannabiscetin.—The flavonol was acetylated by boiling with acetic anhydride and anhydrous sodium acetate. The acetyl

derivative was sparingly soluble in alcohol and freely in acetic anhydride. When crystallised from a mixture of acetic anhydride and alcohol, it came out as fine colourless needles sintering at 210° and melting at 214–15°. One more crystallisation from glacial acetic acid raised the melting point to 215–17°. [Found: C, 56·6; H, 3·9; $C_{15}H_4O_2$ $(OCO\ CH_3)_6$ requires C, 56·8; H, 3·9%.]

Preparation of Hexamethyl Cannabiscetin.—(*a*) The flavonol (1·5 g.) dissolved in methyl alcohol (30 c.c.) was treated with excess of methyl iodide (15 g.) and refluxed on a water-bath. After sometime, methyl alcoholic potash (7 g. of potash in 100 c.c. of methyl alcohol) was slowly added over a period of six hours. The solvent and the excess of the reagent were then distilled off, and water was added to the residue. After cooling, the alkaline liquid was just made acidic, when the ether separated out gradually as a sticky mass. It was purified through repeated crystallisations from alcohol using a little animal charcoal, and was obtained as colourless needles having the appearance of cotton wool.

(*b*) The pigment was also methylated through its acetyl derivative according to the method of Rao and Seshadri.[3] Acetyl cannabiscetin (1 g.) was dissolved in acetone (50 c.c.) and treated with dimethyl sulphate (10 c.c.) and 20% sodium hydroxide (10 c.c.) alternately in small quantities, shaking vigorously after each addition. Finally the mixture was made strongly alkaline by the addition of 5 c.c. more of the alkali. The next day it was refluxed on a water-bath for an hour. The solvent was then driven off and the alkaline solution acidified with dilute hydrochloric acid, when the ether separated out. The solid was filtered and crystallised from dilute alcohol, using a little animal charcoal. The yield was 0·6 g.

The samples as obtained from the above two experiments were found to be identical and melted at 175–76°. [Found in the sample dried at 110°: C, 62·3; H, 5·4; OCH_3 46·1%; $C_{15}H_4O_2(OCH_3)_6$ requires C, 62·7; H, 5·5; OCH_3 46·3%.]

Gossypetone Reaction with the Flavonol.—The substance (0·5 g.) was dissolved in absolute alcohol (8 c.c.) and *p*-benzoquinone (0·2 g.) dissolved in a small amount of alcohol was added to the solution. A dull red crystalline substance began to separate out gradually. When the separation was complete, the solid was filtered and washed with a small quantity of absolute alcohol. [Found: C, 56·8; H, 2·4; $C_{15}H_8O_8$ requires C, 57·0; H, 2·5%.] It had the appearance of red phosphorus. When treated with a drop of dilute alkali, it dissolved producing a blue solution which became red on acidification. On reduction with sulphurous acid, it gave back the original pigment.

Oxidation of the Flavonol: *Isolation of Trimethyl Gallic Acid.*—The flavonol (1 g.) was dissolved in 50% potassium hydroxide (15 c.c.) and left exposed to air for 24 hours with occasional stirring. It was then diluted until the strength of the alkali solution was about 20% and then treated with excess of dimethyl sulphate (15 c.c.) in small quantities. After some time, the excess of the methylating agent was decomposed by heating on the water-bath and the solution acidified with hydrochloric acid. The mixture looked brown and contained a good amount of resin. It was extracted with ether twice and the extract after evaporation left behind a brown viscous liquid which, on leaving in a refrigerator overnight, deposited a colourless crystalline solid. But the substance was still mixed up with a brown viscous resin, and the separation of the two by the ordinary methods of crystallisation was unsuccessful. The mixture was, therefore, pressed on a porous plate, when all the brown viscous liquid was absorbed by the plate, leaving free the colourless crystalline solid. It was scraped out and crystallised from water using a little animal charcoal. It was obtained as fine needles melting at 168–69°, and was found to be identical with the trimethyl ether of gallic acid.

Alkaline Hydrolysis of Hexamethyl Cannabiscetin.—The methyl ether (0·5 g.) was refluxed for 6 hours with 50% potash (20 c.c.) in a silver flask. At the end of this period, a major part of the solid was decomposed. The clear alkaline solution was diluted and then acidified with hydrochloric acid. On extraction with ether, the solution yielded a small amount of trimethyl gallic acid melting at 167–68°. The identification was confirmed by taking the mixed melting point with an authentic sample.

Summary

The colouring matter of the flower petals of *Hibiscus cannabinus* consists mostly of the glucoside cannabiscitrin along with small quantities of the corresponding aglucone cannabiscetin. The properties and reactions of these two substances are described along with those of some of their derivatives.

Cannabiscetin forms a hexaacetate and a hexamethyl ether. It is a flavonol exhibiting similarities with gossypetin and herbacetin particularly in regard to alkali colour reactions and gossypetone reaction. It yields gallic acid on being subjected to alkali fission, its methyl ether producing trimethyl gallic acid. It is, therefore, concluded to be 3 : 5 : 8 : 3′ : 4′ : 5′ hexahydroxy flavone.

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THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID

Part XIII. The Condensation of *o*-, *m*- and *p*- Chloro-benzaldehydes and of *m*-Bromo-benzaldehyde: The Influence of Groups and Comparison with Perkin's Reaction

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Perkin's reaction was probably first used by him (1868) for the preparation of the valuable perfume coumarine. Although cinnamic acid had actually been prepared from benzaldehyde a little earlier, namely, by Bertagini (1856) who had heated the aldehyde with sodium acetate and acetyl chloride in a sealed tube at 120–30°, and by Schiff (1870) who heated benzaldehyde with acetic acid and hydrochloric acid or zinc chloride in a sealed tube at 110–20°, and although controversies regarding the exact mechanism of Perkin's reaction started immediately, the method, with a little modification, soon became popular and attained a classical status in organic laboratory work (1877). It is still of very wide application.

The substitution of acetic acid by malonic acid was the next important step. Indeed it is interesting to realise that it was only in the course of the controversy about the mechanism of the reaction, going on between Perkin and Fittig, that the discovery was made by Stuart in Fittig's laboratory (1883), that the condensation of benzaldehyde to cinnamic acid took place equally well when sodium acetate was replaced by sodium malonate. Stuart also showed that instead of using acetic anhydride at 180°, if glacial acetic acid was used at 100°, better results were obtained. This method was then used by many workers, such as Komnenos (1883), Stuart, (1886), Fittig and Mackenzie (1894) and others. Satisfactory yields were also reported by Michael (1884) who merely heated the aldehyde with malonic acid alone in a sealed tube for several hours at 130–40°.

The next important change, so intimately associated with the name of Knoevenagel (1898), saw the introduction of a base, organic as well as inorganic, in place of acetic acid. His work was at first limited to aromatic aldehydes only (1896) : but it soon extended to aliphatic aldehydes also (1902), and is now well known to travel far beyond this simple aldehyde-malonic acid condensation. The inorganic base was ammonia, in the form

of alcoholic ammonia or ammonium malonate or chloride. The organic bases were either the primary bases like aniline and ethylamine, or the secondary ones like diethylamine and piperidine, or piperidine hydrochloride. The inorganic and the primary organic bases were employed in full molecular or even larger proportions, but the secondary bases were employed in small proportions only. Piperidine in a few drops, the " Knoevenagel's Reagent " is now a very useful ally of the synthetic chemist (1894–1904).

It is remarkable that Knoevenagel did not find much use of pyridine or of any tertiary organic base. It was Verley, according to Boxer and Linstead, who used it first (1899) ; this use was extended widely by Doebner (1900 and onwards) and others. A very important observation is that of Harding and Weizmann (1910), who specially recommended the use of a tertiary base in cases like the preparation of nonylenic acid from heptaldehyde, where Perkin's method gave poor yields of a mixed product and where Knoevenagel's bases gave small yields invariably mixed up with other condensation products (such as those formed from the usual Schiff's condensation of aldehydes with bases). For this and similar condensations, pyridine was generally used in full molecular proportions, or even in greater excess. Staudinger advised the use of anhydrous pyridine in dry ethereal solution: Florence (1927) also recommended the same method for the synthesis of α-β unsaturated aliphatic acids.

The present-day practice in fact favours the combination of pyridine with piperidine, as first recommended by Robinson to Perkin (1924). Haworth, Perkin and Raukin (1924) did not obtain more than a 30% yield of 3:4-methylenedioxycinnamic acid from piperonal by Perkin's method, but found that, following Robinson's suggestion, the yield became ' almost quantitative ' when piperonal, malonic acid and pyridine were taken in 1:2·5:6 mol. proportions with a small amount of piperidine. [About ten years later, the same yield was obtained in this laboratory by Vahidy (1935) when the three were in the proportion of only 1 : 1:0·15 mol.] To-day the proportion of pyridine taken is about 3·5 mols. for 1 of the aldehyde, according to the method established by Robinsin and Shinoda (1925).

The fact that pyridine is also such an excellent solvent for so many substances and should therefore be used in liberal proportions to help the condensation on, and the other fact that as a tertiary base it is less active and strong than piperidine, and may be taken as inert, are probably responsible for the omission, in investigation as well as in literature, of the observation of the catalytic activity of pyridine. The earliest suggestion to this property seems to be contained in the interesting account of Bacharach and Brogan (1928),

who report that a few drops of pyridine used in Perkin's synthesis of cinnamic acid increased the yield to an optimum value of 85%. (Had they used the pyridine alone, without the sodium acetate and acetic anhydride, they might have obtained the still higher yield of about 95%—*vide* Experimental.) A little later, Boxer and Linstead (1931) found that 'Tertiary bases as such have a definite catalytic activity.' A general and systematic study of this catalytic activity has still to be made.

The work of Florence (1927) led Surange in this laboratory in 1929 to apply the pyridine method to a synthesis of aromatic α-β unsaturated acids. When applied to aromatic aldehyde-malonic acid condensation, the original method had to be modified. Nearly quantitative yields were obtained of the corresponding cinnamic acids from benzaldehyde and from *o*-, *m*- and *p*-nitrobenzaldehydes, when the aldehyde, malonic acid and dry pure pyridine were heated together without any solvent on the water-bath for a few hours. Cinnamaldehyde also gave the same high yield, but of a mixture of cinnamalydene-malonic and phenylacrylic acids (unpublished). Surange's failure to obtain any condensation product from hydroxy-benzaldehydes seemed to have been shared by other workers, *viz.*, Dutt, who had used an indefinite pyridine-piperidine mixture (1925).

The problem of the hydroxy-benzaldehydes was reinvestigated by Kurien and Pandya in 1931, who found that only a few drops of pyridine instead of one molecule, were able to do the work, and that in this way pyridine was as good a catalyst as piperidine or other tertiary bases (1934). The work has thereafter been pursued, and most of it published, (i) with a large number of aromatic aldehydes, (ii) with traces of other organic bases as well, most of which were tertiary, and (iii) with not only malonic acid, but also with malonic ester (occasionally) and with malonanilic acid (Mehra, 1938, 1939; Ittyerah, 1941, and Miss Pandya, unpublished) and with the three malon-*o*-, *m*- and *p*-toluidic acids (Ittyerah, unpublished), all of which contain the same reactive methylene group.

In all the above cases pyridine has been found to be a very effecient catalytic agent. Other organic bases too show a similar ability in varying degrees, though one cannot say off-hand as to which base might give the maximum yield in a particular condensation. Thus with salicylaldehyde, it was methylacridine that gave the highest yield (Khan and Kurein, 1935), with piperonal piperidine (Vahidy, 1935), with anisaldehyde isoquinoline (Vahidy, 1936), with *m*-hydroxybenzaldehyde pyridine (Vahidy, 1936), and so on.

When no base and no other chemical agent is present and when the aldehyde and the acid are heated up alone, the condensation proceeds to take

place very slowly, the yield is very much smaller unless the heating is prolonged, and the condensation proceeds without the decarboxylation, the undecarboxylated product being isolable, under suitable conditions, in excellent yields and in a state of purity. In cases when on the aromatic ring the aldehyde has also other groups present, their nature and number have generally a very far-reaching influence on the whole reaction, particularly on its speed and on the yield.

This last point has already been made in an earlier paper by Pandya and Sodhi (1939). Recently Lock and Bayer (1939) have also made a study of the influence of groups on the yiedls obtained during Perkin's reaction under standardised conditions. A comparison can thus be made of the influence of groups in Perkin's reaction with the influence in the pyridine-trace condensation.

Under the conditions chosen, these workers obtain a yield of 49% of cinnamic acid from benzaldehyde. The influence of the halogen atom is stated to produce higher yields of the corresponding cinnamic acids, the position and the number of the halogens making an evident difference. Thus chlorine is stated to give the following yields, which are all higher than that given by the unsubstituted benzaldehyde, *i.e.*, higher than 49% :

Position of chlorine ..	2	3	4	2–3	2–5	2–6	2–3–6	nil
Yield %	71	63	52	62	78	82	66	49

That the yields are higher than those obtained from ordinary unsubstituted benzaldehyde is undoubtedly true, but no other generalisation regarding the influence of number and position would be safe as the figures are so irregular.

In the present paper the condensations of benzaldehyde, of the three chlorobenzaldehydes and of *m*-bromobenzaldehyde with malonic acid and with a trace of pyridine, as well as in the absence of any condensing agent, have been studied. In all the cases, the reactions go very well under the conditions described. Benzaldehyde with only four hours' heating on the water-bath, in the presence of a few drops of pyridine, gave a 95% yield of cinnamic acid. With the entree of a halogen, the reaction was very obviously quickened, so that in the case of the four haloid-benzaldehydes, the reaction was often completed in one hour, the yields were quantitative and the products, therefore, unusually pure. There is no doubt about the accelerating influence of chlorine and bromine here, nor any about this being the best of all the methods found in literature for the preparation of *o*-, *m*- and *p*-chloro- and *m*-bromocinnamic acids.

Originally all these four acids were first prepared by Gabriel (1882) and Gabriel and Herzberg (1883) by a roundabout process of preparing first

the desired nitrocinnamic acid, which was then reduced to the corresponding aminocinnamic acid, which was then diazotized to the diazonium nitrate or sulphate, and then this was warmed with fuming hydrogen chloride or with ten parts of strong hydrobromic acid. *o*-Chlorocinnamic acid was obtained a little later by Stuart (1888) from *o*-chloro-benzalmalonic acid, itself prepared by the 'Stuart-method' of heating *o*-chlorobenzaldehyde with malonic acid and glacial acetic acid. Perkin's method was first applied to *m*-bromobenzaldehyde by Miller and Rohde (1890) who, after heating the Perkin mixture at 140–50° for as many as twenty hours, obtained a 73% yield of *m*-bromocinnamic acid. Perkin's method was applied to the three chlorobenzaldehydes by Meyer and Beer (1913) and by Meyer, Beer and Lasch (1913); these have been confirmed by Lock and Bayer (1939) and have been stated above. Neither this nor any other group of workers has referred to the condensation of *m*-bromobenzaldehyde by Perkin's method under the standardised conditions, though they make a comparison of all the *p*-haloid-benzaldehydes: thus the yields of *p*-bromocinnamic acid from *p*-bromobenzaldehyde in two experiments (Perkin) are given as 48·6 and 52·6% respectively. This is about the same as their yield of the *p*-chlorocinnamic acid. Could we thus assume that the yield of the *m*-chlorocinnamic acid would be about the same as the yield of the *m*-bromocinnamic acid, their yield of the latter might then be about 63%. Against this, the yields of these four haloid-cinnamic acids obtained by our pyridine method range between 97 and 99%.

All the four haloid-benzaldehydes also condense with malonic acid when heated alone with them, giving, under carefully controlled conditions, nearly quantitative yields of the corresponding haloid-benzalidene-malonic acid: of these only one, the *o*-chlorobenzalmalonic acid, has been previously described (Stuart, 1888).

The halogen undoubtedly increases the yield in the Perkin as well as in the pyridine-trace condensations, but the influence of the position of the halogen does not seem to coincide in both. The *p*-chlorine which seems to be most helpful in the pyridine-trace condensation appears to be the reverse in the Perkin condensation.

The three chlorobenzaldehydes undergo a similar condensation with malonanilic acid, but the details of this must find place in a separate paper.

Experimental

Condensation of Benzaldehyde:

In the Presence of a Trace of Pyridine.—1·06 g. benzaldehyde, 1·04 g. dry malonic acid and 0·13 g. pyridine, purified in the usual way, (1 : 1 : 0·15 mol.) were heated together on water-bath for four hours ; the mixture

soon became a homogeneous liquid and effervescence commenced within ten minutes of the heating and continued for about an hour. Cinnamic acid came out at the end in white crystals, which were extracted as usual and which then melted at 133° and weighed 1·4 g. or 94·6% of theory. In another experiment the heating was stopped after two hours only ; the yield was 1·3 g. or 87·8%. This is considerably greater than that of Bayer and Lock, and is higher than the highest yield claimed under Perkin's method under the most favourable conditions.

Without any Condensing Agent.—The same amounts of benzaldehyde and malonic acid were heated alone separately on water-bath in three different flasks that were heated respectively for four, six and eight hours. The mixture did not become a homogeneous liquid and no effervescence was observed. After about ten minutes a pinkish colour began to make its appearance and after one hour the whole mixture had become a pinkish solid mass. At the end of the heating, the benzalmalonic acid was extracted as usual by means of sodium carbonate and hydrochloric acid. It melted at 195–96° and weighed 1·5, 1·5 and 1·3 g. respectively, the yield thus being 78, 78 and 73% respectively.

The Condensation of p-*Chlorobenzaldehyde with Malonic Acid*

(*i*) *In the Presence of a Trace of Pyridine*:

The Materials.—The *p*-chlorobenzaldehyde was very pure and melted at 47°. (Literature gives 47°, 48°, 49°, Beilstein.) The malonic acid, Merck, Pure for Scientic Purposes, was powdered, dried at 100° and kept in a desiccator. Pyridine, Extra Pure, Merck, or Purest, Schering-Kahlbaum, was kept over sticks of pure caustic potash for several days and fresh-distilled (b.p. 114–115°).

p-Chlorocinnamic Acid.—1·04 g. malonic acid, 1·4 g. *p*-chlorobenzaldehyde and 0·14 c.c. pyridine (1 : 1 : 0·16 mol. proportions, 1/100th mol.wt.) were mixed in a flask and heated on water-bath without a condenser for four hours. The reaction started very quickly: in two minutes the whole fused to a homogeneous liquid and effervescence commenced. In another five minutes, a cream-coloured solid mass made its appearance, and the whole mass had become perfectly solid long before the heating was stopped. It was allowed to cool, treated with 10% sodium carbonate solution and the small amount of the residue was removed by filtration. As the residue, however, gave the same high melting-point as the crude product, namely, 235°, it was clear that it was not the unreacted aldehyde, melting at 47° : in fact treatment with hot sodium carbonate solution dissolved it completely, and, on acidification of both the extracts, the same white precipitate was obtained.

On washing with water it melted at 245°. This must be highly pure as its melting-point, even before recrystallisation, was higher than that given in literature (240–42°, Gabriel and Herzberg, *loc. cit.*).

The *p*-chlorocinnamic acid was a cream-coloured indistinct crystalline mass, very slightly soluble in water, alcohol, benzene, chloroform or carbon tetrachloride in the cold, slightly soluble in hot water or hot benzene, and soluble in acetone or in hot alcohol. Recrystallisation raised its melting-point to 246–47°, and it came out in long silky needles. It at once decolourized Baeyer's reagent. Yield 1·8 g. (theoretical yield = 1·825 g.).

In another experiment, the reaction mixture, of the same composition as above, was kept on the water-bath for only one hour instead of four, as the reaction seemed then to be complete. No aldehyde was recovered back, the *p*-chlorocinnamic acid was sufficiently pure, as, after a washing with water, it melted at 244–245°, and it was not necessary to extract it with sodium carbonate solution or to prepare the not very soluble sodium salt. The yield was again quantitative, and the melting-point, after recrystalliastion, 247°. (Lock and Bayer give the same.)

(*ii*) *In the Absence of any Condensing Agent*:

p-Chlorobenzalmalonic Acid.—The aldehyde and the acid (1/100th mol.) were heated alone, as before, on water-bath. The reaction was much slower ; it required an hour's heating to change the whole to a clear liquid and there was no effervescence, even during eight hours' heating. Slowly a solid began to be formed and took several hours to be completed. The crude product was treated with cold 10% sodium carbonate solution which dissolved the whole and left no residue. Acidification with hydrochloric acid yielded a slightly cream-coloured solid, which was filtered and washed with cold water. The acid immediately decolourised Bayer's reagent, was very little soluble in cold water, moderately soluble in excess of hot water and easily soluble in alcohol or acetone even in the cold. Recrystallised from dilute alcohol, or dissolved in minimum quantity of alcohol and precipitated on scratching after the addition of a large amount of water, it came out in white needles, and after drying in the desiccator for 24 hours, it melted with effervescence at 197–98°. The yield was 1·8 g. or about 80% of theory.

In a second experiment it was observed that the reaction was really completed in four hours and the yield then—2·25 g.—was quantitative. Further confirmation of its identity was obtained from analysis. (Cl, found, by Piria and Schiff's method: 15·63%; $C_{10}H_7O_4Cl$ requires 15·67%. Equivalent weight by titration, found = 113·2: *p*-chlorobenzalmalonic acid requires 113–25. Molecular weight, silver salt, found 226·4; theory requires 226·5.)

(*iii*) *Condensation with Ethyl Malonate :*

3·2 g. Ethyl malonate, Schering, Extra Pure, fresh redistilled, 2·8 g. *p*-chlorobenzaldehyde and 0·28 c.c. pyridine (1/50th mol., 1 : 1 : 0·16) were mixed and heated together on water-bath for 26 hours. White needle crystals separated out of the liquid on cooling. They were filtered off from the mother-liquid, washed, dried on a porous plate, washed on the porous plate with a little water and dried : m.p. 235°. Insoluble in water and easily soluble in alcohol, the substance had the characteristic fragrant smell of esters. Yield 1·0 g. (18% of theory). Recrystallised from alcohol, it melted at 237°. It instantly decolorised Baeyer's reagent. (Cl, Found : 12·09%; Ethyl *p*-chlorobenzylidenemalonate, $C_{14}H_5O_4Cl$ requires 12·56%.)

The Condensation of m-*Chlorobenzaldehyde with Malonic Acid*

(*i*) *In the Presence of a Trace of Pyridine*:—

m-*Chlorocinnamic Acid.*—The aldehyde, the acid and pyridine were taken in the same proportion as above and heated on the water-bath. The reaction was slower distinctly than was observed with the *p*-isomer. It took ten minutes to liquefy completely and the effervescence continued much longer. In half an hour, the whole became solid again and the heating was stopped after one hour. The crude product was white and melted at 159°. It dissolved in sodium carbonate solution without leaving a residue, and *m*-chlorocinnamic acid was easily recovered on acidification of the sodium salt solution. After filtration and washing with water, it melted at 160°. It was readily soluble in cold acetone, soluble in alcohol and in hot benzene, less in hot water, still less in cold benzene. Recrystallised from alcohol repeatedly, the melting point remained stationary at 163°. Gabriel and Herzberg describe it as indistinct yellow, melting at 176°, which is not confirmed: other workers, however, give the melting point at 165° (Heilbron, *Dictionary of Organic Chemistry*, 1, 276). It decolorised Baeyer's reagent. Yield 1·8 g. (theoretical 1·825 g. from 1·4 g. of the aldehyde).

(*ii*) *Condensation without any Condensing Agent*:

m-*Chlorobenzyilidenemalonic Acid.*—1·04 g. Malonic acid and 1·4 g. *m*-chlorobenzaldehyde were heated alone on the water-bath for four hours. A solid with a pale pink tint had been formed at the end, which dissolved completely in sodium carbonate solution ; from this, on acidification, a cream-coloured solid was obtained which decolorised Baeyer's reagent, and which, on recrystallisation from alcohol, melted at 184–86°. It weighed 2·2 g. (theoretical yield = 2·25 g.). (Equivalent weight, found by titration with standard alkali, 113·6; the dibasic acid $C_{10}H_7O_4Cl$ requires 113·25. Cl, found: 15·29%; the chlorobenzylidene-malonic acid requires 15·67%.)

The Condensation of o-*Chlorobenzaldehyde with Malonic Acid*

(*i*) *In the Presence of a Trace of Pyridine*:

o-Chlorocinnamic Acid.—The three were heated in the usual proportions on a water-bath. In ten minutes the reaction mixture became a clear liquid and effervescence started. Within half an hour a white solid began to be formed. After four hours' heating, the cold product was treated with a little cold water and a little ether. The remaining crude product melted at 207° and, when recrystallised from alcohol, melted at 210°. Further recrystallisations raised the melting point to 211–212°. The *o*-chlorocinnamic acid was then in the form of colourless needles. In literature Gabriel and Herzberg (1883) have described it as indistinct yellow, melting at 200°; Stoermer (1911) gives 205° as the m.p. and Lasch (1913) gives 211°. The yield was 1·8 g. (the theoretical is 1·825 g.).

Condensation without any Condensing Agent : o-*Chloro-benzalmalonic Acid.*—1·4 g. *o*-chlorobenzaldehyde and 1·04 g. malonic acid were heated alone on a water-bath for six hours. There was no effervescence, but the reacting mass began to solidify after only one hour's heating. The product was washed with water and dried: it melted at 185°, and, when crystallised from hot alcohol, it came out in white crystals, melting at 192°: Stuart also gives 192°. It weighed 2·1 g. (93% of theory).

Condensation of m-*Bromobenzaldehyde* :

In the Presence of Pyridine.—0·925 g. *m*-Bromobenzaldehyde, 0·52 g. malonic acid and 0·07 g. pyridine were heated together on a water-bath. The mixture immediately became a clear liquid and effervescence started within five minutes. Within half an hour a pale yellow solid began to come out in the liquid. In two concordant experiments, the total heating was two and four hours respectively. The solid dissolved completely in sodium carbonate solution, and the addition of concentrated hydrochloric acid drop by drop brought about the separation of white crystals of *m*-bromocinnamic acid. The yields were 1·0 and 1·1 g. respectively, corresponding to 88·5 and 97% of the theoretical. The crude product melted at 170°, the recrystallised at 174°.

Condensation in the Absence of a Condensing Agent: m-*Bromobenzal-malonic Acid.*—1·04 g. malonic acid and 1·85 g. *m*-bromobenzaldehyde were heated alone on a water-bath in two separate flasks for four and eight hours respectively. The reacting mass did not liquefy nor effervesced, but in about 45 minutes a pale yellow solid began to emerge in view, till, as usual, the whole mass set as a solid. This was treated with cold sodium carbonate solution, the residual resinous matter filtered off and *m*-bromobenzalmalonic

acid precipitated as a white shining crystalline mass by careful treatment with strong hydrochloric acid. The acid was very soluble in cold alcohol and acetone, and was recrystallised from benzene or dilute alcohol or a benzene-alcohol mixture. It melted with effervescence at 192°. The yields were 2·4 and 2·7 g. or 87 and 99% of theory, respectively.

[Bromine found = 29·86%: bromobenzalmalonic acid $C_{10}H_7O_4Br$ requires 29·52%. Equivalent weight found by titration = 135·4 ; required = 135·5.]

Summary

1. Benzaldehyde and four haloid-benzaldehydes have been condensed with malonic acid, in the presence of a trace of pyridine as well as in the entire absence of any condensing agent.

2. The yields in all cases have been excellent, in some cases almost quantitative.

3. Chlorine and bromine have undoubtedly accelerated the condensation and increased the yields.

4. Compared to the yields obtained by Perkin's method, these yields are very superior, the condensations quicker and the products cleaner.

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A NOTE ON GLABRIN, A NEW COMPONENT OF THE SEEDS OF *PONGAMIA GLABRA*

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(Communicated by Prof. T. R. Seshadri)

In a previous communication,[1] it was reported that by the extraction of the seed-cake of *Pongamia glabra* higher fatty acids along with some karanjin could be obtained. In our search for the presence of any further insecticidal principles, the cake was next subjected to extraction with alcohol and from this was obtained a small yield of a crystalline nitrogenous substance. Since its properties and reactions are not identical with any known compound, it is considered to be a new substance and it has been named Glabrin. It is best obtained from mature seeds since otherwise it has been noticed that the yield becomes practically negligible.

Glabrin melts at 290° with decomposition and has the empirical formula $C_7H_{14}NO_4$. It is very sparingly soluble in all the organic solvents. On the other hand it goes readily into solution in water. It is optically active and exhibits all the properties of α-amino acids of the dicarboxylic type, the most important being the ninhydrin test and copper salt formation. Attempts to determine the molecular weight have not been quite successful. However, titration with alkali without formalin and with the addition of formalin (Sorensen's titration) fixes the minimum molecular weight at 580 and consequently the molecular formula may be tentatively given as $C_{21}H_{42}N_3O_{12}$. Attempts to hydrolyse it using hydrochloric acid were not successful.

Since the yield of the substance is very low (0·1%), its extraction extremely slow and since it has no marked physiological properties, no further detailed work has been undertaken.

Experimental

The seed-cake of *Pongamia glabra* (3 kg.) left behind after extraction of the seeds with petroleum ether was freed from the solvent and was subsequently extracted with methylated spirits in a continuous extraction apparatus. The process was very slow and therefore it was continued for 60 hours. The receiver containing the extract was set aside for a few days to complete the deposition of the crystalline solid that began to separate. It was then

filtered and washed with light petroleum. On careful examination it was found to be a mixture and that the components could be separated easily because of their differences in solubility in alcohol. The one that went easily into solution in hot alcohol was identical with karanjin in all its properties. The second which was sparingly soluble in all the common organic solvents could not be recrystallised in the normal manner; but, however, advantage was taken of its solubility in water. The substance (3 g.) was dissolved in the minimum amount of water (10 c.c.) and then filtered so as to remove all the adhering impurities. The clear solution was then decolourised with vegetable carbon. Since attempts to obtain the substance in a pure condition, as for example by evaporating the aqueous solution, were unsuccessful, alcohol was added to the colourless aqueous solution in order to precipitate the substance. As the addition of alcohol did not bring about the separation of the substance, a large excess of ether was added to the aqueous alcoholic solution. Glabrin separated out as a shining colourless crystalline solid (rectangular plates). The mixture was allowed to remain overnight to facilitate the complete precipitation of the substance and was then filtered and air-dried.

Glabrin was found to melt with decomposition at 290° and contain nitrogen. [Found: C, 47·8; H, 8·0; N, 8·0%; $C_7H_{14}NO_4$ requires C, 47·7; H, 8·0; N, 8·0%]. It went easily into solution in aqueous alkalies and acids. Further, its aqueous solution gave acidic reaction to phenolphthalein and litmus and produced effervescence with sodium carbonate and bicarbonate, indicating thereby the presence of one or more free carboxylic groups in the molecule. It exhibited optical activity and had a specific rotation, – 56·1°.

When an aqueous solution of glabrin was boiled with alkali, no ammonia was evolved. Further, it did not produce any precipitate with Nessler's reagent. This eliminates the possibility of glabrin being an ammonium salt. However, it produced a deep blue colour when a pinch of copper carbonate was added to its aqueous solution and the resulting copper salt was found to crystallise in leaflets. It did not give the tests for an amino group. But on reduction with sodium and alcohol, it responded to the carbylamine reaction. In this connection it has been found that aspartic acid also does not directly give the carbylamine reaction. Glabrin gave a blue colour when boiled with ninhydrin. This is a test which all acids having a free amino group in the α-position to a free carboxylic group give. It is known that ninhydrin reaction is very sensitive in cases of amino acids and that ammonium salts also give a positive reaction provided the concentrations are sufficiently high. But the latter possibility has been ruled out as already described.

A solution of glabrin in water was titrated with standard alkali without and with the addition of formalin. The amount of alkali consumed in the latter titration was double that in the former. This clearly indicates the presence of one amino group and two carboxylic groups in the molecule. The calculated equivalent weight of the substance from the above data was 580.

Glabrin was subjected to acid hydrolysis using 20% hydrochloric acid with a view to obtain simpler products which could be more easily identified. But the resulting product was found to melt at the same temperature as glabrin and the mixed melting point of the substance was not depressed.

The toxic effect of glabrin on fish was studied by placing small fresh water fish in a solution of the substance in water (1 g. in 1000 c.c.). As there was no perceptible change in the fish even after 24 hours, it was concluded that glabrin is non-toxic fish.

The authors wish to express their gratitude to Prof. T. R. Seshadri for his interest and guidance throughout the work.

Summary

A new nitrogenous substance has been isolated from the seeds of *Pongamia glabra* and has been named Glabrin. Its composition and properties have been studied. It seems to belong to the group of complex amino acids and is non-toxic to fish.

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SYNTHETICAL EXPERIMENTS IN THE GROUP OF SYMPATHOMIMETICS—PART III

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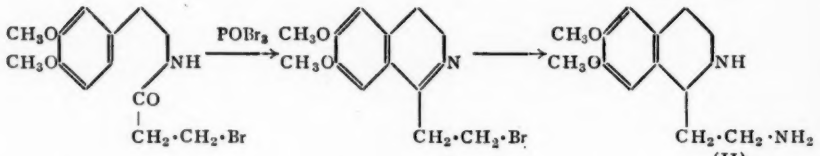
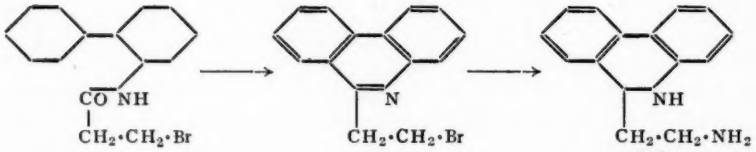
In continuation of the study[1] on the relationship between chemical constitution and physiological activity of sympathomimetic amines derived from various ring-systems, one member of the group of β, β-bis-aryl-β-hydroxy ethylamines belonging to the phenanthrene series, *viz.*, β, β-bis (9-phenanthryl)-β-hydroxy ethylamine (I), has now been synthesised in the usual way.[1,2] The present study also included the synthesis of a β-aminoethyl isoquinoline (II) and a β-aminoethyl phenanthridine (III) on the following lines:

$$9\text{—}C_{14}H_9MgBr + H_2N\cdot CH_2\cdot CO_2Et,\ HCl \longrightarrow (9\text{—}C_{14}H_9\text{—})_2C(OH)\cdot CH_2\cdot NH_2$$

(I)

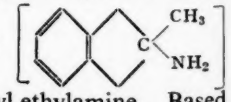


(II)



(III)

The scheme for the synthesis of compounds (II) and (III) had, however, to be ultimately abandoned owing to very low yields of the intermediate β-bromoethyl isoquinoline with the former and the failure of the cyclisation to 9-β-bromoethyl phenanthridine in the case of the latter.

A survey of the literature on sympathomimetics brought to light the highly significant observation[3] that methylaminohydrindene  is intensely active by virtue of its being doubly a β-phenyl ethylamine. Based

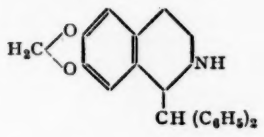
on the above finding and actuated by considerations of the relative ease with which such bodies could be synthesised, the following compounds, possessing the requisite structure necessary for sympathomimetic activity, have been prepared:

$(C_6H_5)_2CH\cdot CH_2\cdot NH_2$
(IV)

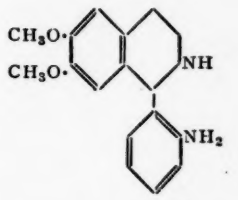
$(C_6H_5)_2C(OH)\cdot CH_2\cdot NH_2$
(V)

$(C_6H_5)_2C(OH)\cdot CH(NH_2)\cdot CH_2\cdot C_6H_5$
(VI)

$C_6H_5\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot C_6H_5$
(VII)



(VIII)



(IX)

A close examination of the formulæ-picture of the compounds IV to VIII reveals the active groups, Ar. C.C.N, being repeated in their molecules. The compound (IX), in addition to falling structurally in the class of the sympathomimetic norhydro hydrastinines, constitutes an interesting variation of a β-amino ethyl tetrahydro isoquinoline, wherein the α- and β-carbon atoms are linked by a double bond and form part of an aromatic nucleus.

A few of these compounds (IV, V and VI), although known in literature, were included for purposes of a comparative pharmacological study in progress elsewhere. β, β-Diphenyl ethylamine[4] (IV) has advantageously been prepared now in good yields by the Hoffmann degradation of β, β-diphenyl propionamide.[5] The customary methods were adopted for the synthesis of the other members of the group.

The results of pharmacological examination of about twenty final compounds, hitherto synthesised, compared to tyramin as control, have been reserved for a future communication.

Experimental

β, β-Bis-(9-phenanthryl)-β-hydroxyethylamine (I) hydrochloride.—A Grignard solution was prepared according to Bachmann[6] from magnesium (3·54 g.), 9-bromophenanthrene[7] (38·3 g.) and a mixture of ether (100 c.c.) and benzene (100 c.c.) in an atmosphere of dry nitrogen. Glycine ester hydrochloride (6·7 g.) was added and the mixture refluxed for 1 hour on the water-bath, cooled, decomposed with dilute hydrochloric acid and the

separated solid filtered. The hydrochloride was recrystallised once from alcohol-ether and once from dilute hydrochloric acid as almost colourless needles, m.p. 239–40° (dec.). [Found: Cl, 8·23; $C_{30}H_{24}ONCl$ requires Cl, 7·90%.]

The *picrate* was obtained as greenish-yellow needles, m.p. 209–10° (dec.). [Found: N, 8·36; $C_{36}H_{26}O_8N_4$ requires N, 8·73%.]

1-β-Bromoethyl-3 : 4-dihydro-6 : 7-dimethoxy isoquinoline:

β-Bromopropionyl chloride.—β-Bromopropionic acid[8] (20 g.) and thionyl chloride (18 c.c.) were heated together on the water-bath for 2 hours, and the reaction mixture fractionated. The acid chloride was obtained as an almost colourless, lachrymatric oil, b.p. 115-17°/30 mm. Yield 15·4 g.

β-Bromopropionyl homoveratrylamide.—A mixture of homoveratrylamine[9] (5 g.) and β-bromopropionyl chloride (5 g.) in a little petrol was strongly cooled and gradually treated with dilute sodium carbonate under shaking. The amide separated from water in long, colourless, prismatic needles, m.p. 120–21°; yield 2·5 g. [Found: N, 4·28; $C_{13}H_{18}O_3NBr$ requires N, 4·43%.]

1-β-Bromoethyl-3 : 4-dihydro-6 : 7-dimethoxy isoquinoline.—The above amide (2·4 g.) in chloroform (20 c.c.) was allowed to react at the room temperature with phosphorus oxybromide (10 g.) for 1 week with the exclusion of moisture. The isoquinoline was obtained as a thick brown oil; yield, 0·4 g. One half of the unreacted amide was recovered at the end of the experiment. The *picrate* separated from acetic acid as a yellow powder, decomposing at 166–68°. [Found: N, 10·12; $C_{19}H_{19}O_9N_4Br$ requires N, 10·63%.]

β-Bromopropionyl-o-amino-diphenyl, obtained in 50% yield, crystallised from alcohol in colourless needles, m.p. 118°. [Found: N, 4·80; $C_{15}H_{14}ONBr$ requires N, 4·83%.]

β, β-Diphenyl ethylamine (IV) hydrochloride:

β, β-Diphenyl propionamide.[5]—β, β-Diphenyl propionic acid[10] (15 g.) in chloroform (50 c.c.) was treated with thionyl chloride (10 c.c.), the mixture allowed to stand overnight and gradually added to well-cooled liquor ammonia (75 c.c.) containing a little sodium hydroxide (5 g.). The amide, isolated in the usual way, was obtained in a yield of 12 g., m.p. 124–25°. [Found: N, 6·34; $C_{15}H_{15}ON$ requires N, 6·22%.]

β, β-Diphenyl ethylamine[4] *hydrochloride.*—The above amide (12 g.) was shaken with a cold solution of sodium hypochlorite (from 4 g. of potassium permanganate and 125 c.c. of 10% sodium hydroxide). The temperature was gradually raised to 65° and maintained at 65–70° for 1 hour, cooled, treated

with solid potassium hydroxide (45 g.), heated at 70–80° for half-an-hour, cooled and thoroughly extracted with ether. The ethereal extract was washed and extracted with dilute hydrochloric acid. The aqueous acid solution was evaporated to dryness on the water-bath and the residual hydrochloride recrystallised from alcohol-ether in colourless needles, m.p. 256°; yield, 5 g. [Found: Cl, 14·94; $C_{14}H_{16}NCl$ requires Cl, 15·20%.]

The *picrate* separated from alcohol as greenish-yellow crystals, m.p. 210° (dec.). [Found: N, 13·10; $C_{20}H_{18}O_7N_4$ requires N, 13·14%.]

β, β-Diphenyl-β-hydroxy-ethylamine (*V*) *hydrochloride*, prepared according to Thomas and Bettzieche[2] from phenyl magnesium bromide and glycine ester hydrochloride, crystallised from alcohol-ether in colourless needles, m.p. 191° (dec.). [Found: Cl, 13·85; $C_{14}H_{16}ONCl$ requires Cl, 14·23%.]

The *picrate* separated from alcohol in yellow needles, m.p. 179° (dec.). [Found: N, 12·95; $C_{20}H_{18}O_8N_4$ requires N, 12·67%.]

β, β-Diphenyl-β-hydroxy-α-benzyl ethylamine (*VI*) *hydrochloride*,[2] obtained by reaction of phenyl magnesium bromide (from 35 g. of bromobenzene) and β-phenylalanine ester hydrochloride[11] (6 g.) in fairly good yield (4·5 g.), recrystallised from alcohol-ether as a white crystalline powder, m.p. 225–26° (dec.).

Dibenzylaminomethane (*VII*) *hydrochloride*.—The attempt to reduce dibenzyl ketoxime[12] with sodium amalgam to the desired amine was unsuccessful due, probably, to strong steric hindrance. The amine was, however, prepared by the modified Leuckart method.[13]

Dibenzyl ketone (30 g.) and formamide (20–25 c.c.) were heated together at 175–85° for 8 hours and, thereafter, worked up in the usual way.

The *hydrochloride* recrystallised from dilute hydrochloric acid or alcohol-ether in colourless needles, m.p. 200–01°; yield 25 g. [Found: C, 72·14; H, 6·85; Cl, 14·20; $C_{15}H_{18}NCl$ requires C, 72·73; H, 7·27; Cl, 14·34%.]

The *N-formyl-derivative* separated from alcohol in colourless needles, m.p. 88-89°. [Found: N, 5·57; $C_{16}H_{17}ON$ requires N, 5·86%.]

The *picrate* separated from alcohol in yellow plates, m.p. 191–92° (dec.). [Found: N, 12·59; $C_{21}H_{20}O_7N_4$ requires N, 12·70%.]

1-*Diphenylmethyl*-1 : 2 : 3 : 4-*tetrahydro*-6 : 7-*methylenedioxy isoquinoline* (*VIII*) *hydrochloride*:

Diphenylacetyl homopiperonylamide.—Homopiperonyl amine[14] (3·3 g.) and a solution of the crude diphenyl acetyl chloride (from 4·5 g. of the acid and excess of thionyl chloride) in petroleum-ether were condensed together

in the presence of dilute alkali. The separated amide was filtered and recrystallised from alcohol in long, colourless needles, m.p. 139–40°; yield, 2·6 g. [Found: N, 3·84; $C_{23}H_{21}O_3N$ requires N, 3·90%.]

1-*Diphenylmethyl*-3: 4-*dihydro*-6: 7-*methylenedioxy isoquinoline*.—A mixture of the above amide (2·5 g.), phosphorus oxychloride (7·5 c.c.) and dry toluene (20 c.c.) was gently refluxed on the sand-bath for 1½ hours with the exclusion of the moisture, cooled and poured on to crushed ice with stirring. The solution, after freeing from non-basic impurities by extraction with ether, was cooled in ice, basified with excess of sodium hydroxide and the separated solid filtered. The dihydro isoquinoline recrystallised from alcohol in colourless needles, m.p. 125–26°, after sintering at 120°; yield, 2·2 g. [Found : N, 4·01; $C_{23}H_{19}O_2N$ requires N, 4·11%.]

1-*Diphenylmethyl*-1: 2: 3: 4-*tetrahydro*-6: 7-*methylenedioxy isoquinoline hydrochloride*.—The crude dihydro base (2 g.), zinc dust (10 g.) and dilute sulphuric acid (60 c.c. of 1: 4) were heated together on the boiling water-bath for 4 hours, filtered, cooled, basified with a large excess of ammonia and extracted with ether. The isoquinoline was purified twice through a dilute hydrochloric acid solution and the hydrochloride, obtained by evaporation of a dilute acid solution, crystallised from alcohol-ether in faintly yellowish, prismatic needles, m.p. 239° (dec.); yield 1·6 g. [Found: Cl, 10·10; $C_{23}H_{22}O_2NCl$ requires Cl, 9·34%.]

The *N-acetyl derivative* separated from alcohol in colourless needles, m.p. 172°. [Found: C, 77·26; H, 5·43; $C_{25}H_{23}O_3N$ requires C, 77·91; H, 5·97%.]

The *picrate* crystallised from dilute acetic acid in yellow needles, m.p. 212–13° (dec.). [Found: N, 10·32; $C_{29}H_{24}O_9N$ requires N, 10·15%.]

1-(o-*Amino*)-*phenyl*-1: 2: 3: 4-*tetrahydro*-6: 7-*dimethoxy isoquinoline* (IX) *hydrochloride*:

o-*Nitrobenzoyl homoveratrylamide*.—Homoveratryl amine (2·4 g.) by condensation with *o*-nitrobenzoyl chloride in the usual way gave the crude amide (4·6 g., m.p. 138–40°). The amide crystallised from alcohol in colourless, silky needles, m.p. 142°. [Found: N, 8·44; $C_{17}H_{17}O_5N_2$ requires N, 8·51%.]

1-(o-*Nitro*)-*phenyl*-3: 4-*dihydro*-6: 7-*dimethoxy isoquinoline*.—The crude amide (4·5 g.), phosphorous oxychloride (15 c.c.) and toluene (40 c.c.) were gently refluxed together for 1 hour and worked up as usual. The isoquinoline separated from alcohol in faint-yellow needles, m.p. 117°, after slight

shrinking at 112°; yield 4·2 g. [Found: N, 8·87; $C_{17}H_{15}O_4N_2$ requires N, 9·00%.]

1-(o-*Amino*)-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-6 : 7-*dimethoxy isoquinoline.*—The nitro dihydro base (1 g.), zinc dust (10 g.) and dilute sulphuric acid (60 c.c. of 1 : 4-) were heated together on the boiling water-bath for 6 hours and worked up. The base separated from alcohol as hard, colourless crystals, m.p. 162°. [Found: C, 72·21; H, 6·36; $C_{17}H_{19}O_2N_2$ requires C, 72·07; H, 6·71%.]

The *monohydrochloride* separated from alcohol-ether in clusters of colourless needles, m.p. 189° (dec.), after sintering at 183°. [Found: Cl, 11·50; $C_{17}H_{20}O_2N_2Cl$ requires Cl, 11·06; %.]

The *diacetyl derivative* crystallised from alcohol as colourless needles, m.p. 196°. [Found: N, 7·42; $C_{21}H_{23}O_4N_2$ requires N, 7·63%.]

Summary

With the object of studying the relationship between chemical constitution and physiological activity of sympathomimetically active amines, one member of the group $Ar_2 : C(OH) \cdot CH_2NH_2$, belonging to the phenanthrene series has been synthesised.

A number of simple bases derived from benzene and the isoquinoline ring-systems, possessing the requisite structure for sympathomimecity, have also been prepared for purposes of a comparative pharmacological study.

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EINSTEIN SPACES ADMITTING THE LORENTZ GROUP*

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I. It was shown by Kosambi that the classical theories of relativity could be generalized by direct application of the Lorentz group to the trajectories. This gave rise to four-dimensional path-spaces, K_4

$$\ddot{x}^i - p^i \frac{Y}{X} G(\zeta) + 2\dot{x}^i \frac{Z}{X} \gamma(X, \zeta) = 0,^1 \qquad (1)$$

$(i = 0, 1, 2, 3;\ \gamma \text{ arbitrary}),$

where Kosambi's notations are used:†

$$g_{00} = -g_{11} = -g_{22} = -g_{33} = 1, \quad g_{ij} = 0 \quad i \neq j,$$

$$p^i = x^i, \quad p_j = g_{jr}p^r, \quad X = g_{ij}p^i p^j, \quad Y = g_{ij}\dot{x}^i \dot{x}^j,$$

$$Z = g_{ij}\,\dot{x}^i p^j, \quad \xi = \frac{Z^2}{XY}.$$

It has also been shown by the same author in the form of a theorem that:

The most general path equations derivable from three-dimensional observations and admitting the Lorentz group are :

$$\ddot{x}^i - p^i Y G\left(X, \frac{Z^2}{Y}\right) + \dot{x}^i Z \gamma\left(X, \frac{Z^2}{Y}\right) = 0^2. \qquad (2)$$

The purpose of this note is to discuss the conditions under which the most general Riemannian space, admitting the Lorentz group, can be an Einstein space when (i) the invariant R of the corresponding Ricci tensor survives, (ii) the invariant R vanishes.

In what follows we shall consider an n-dimensional Riemannian space because it has been pointed out by Kosambi[3] that if we extend our treatment to more than four-dimensions, with the corresponding extended Lorentz group, the results are valid also for n-dimensional space.

* It is a great pleasure to me to thank Prof. D. D. Kosambi for his kind suggestion and criticism during the course of this investigation. I have made free use of his unpublished manuscript entitled : 'Path-equations admitting the Lorentz group II'.

† Besides these notations I use the universal notations as given in Eisenhart's "Riemannian geometry".

II. The most general Riemannian metric, admitting the Lorentz group has the form

$$f=\frac{\alpha Y}{X}+\frac{\beta Z^2}{X^2}=\left(\frac{\alpha g_{ij}}{X}+\frac{\beta p_i p_j}{X^2}\right)\dot{x}^i\dot{x}^j; \tag{3}$$

α, β are functions of X,

subject to the following conditions of non-degeneracy:

$$\left|\frac{\alpha g_{ij}}{X}+\frac{\beta p_i p_j}{X^2}\right|=-\frac{\alpha^3(\alpha+\beta)}{X^4}\neq 0^3 \tag{4}$$

If we put

$$\frac{\alpha'}{\alpha+\beta}-1=A,\ \frac{2\alpha'\beta-\alpha\beta'}{\alpha(\alpha+\beta)}=B,\ \frac{\alpha'}{\alpha}-1=C, \tag{5}$$

where *dash* indicates differentiation with respect to *log X*, the geodesics of (3) are given by

$$\ddot{x}^i-p^i\left(\frac{AY}{X}+\frac{BZ^2}{X^2}\right)+2C\dot{x}^i\frac{Z}{X}=0^3 \tag{6}$$

It is obvious that equations (6) are the particular cases of equations (1) and (2).

Taking $$\bar{g}_{ij}=\frac{\alpha g_{ij}}{X}+\frac{\beta p_i p_j}{X^2}$$

to be the fundamental metric tensor, we get the following invariants (the bar, put above, indicates that these invariants are derived from $\bar{g}_{ij}$ as the fundamental tensor).

$$\bar{R}^i{}_{jkl}=\frac{U}{\alpha\gamma X}(\delta^i{}_l g_{jk}-\delta^i{}_k g_{jl})+\frac{S}{\alpha^2\gamma X^2}(\delta^i{}_k p_j p_l-\delta^i{}_l p_j p_k)$$
$$+\frac{Q}{\alpha\gamma^2 X^2}(p^i p_l g_{jk}-p^i p_k g_{jl}), \tag{7, a}$$

$$\bar{R}_{ij\,kl}=\frac{U}{\gamma X^2}(g_{il}g_{jk}-g_{ik}g_{jl})+\frac{Q}{\alpha\gamma X^3}(p_i p_l g_{jk}-p_i p_k g_{jl})$$
$$+\frac{(\gamma-\alpha)U}{\alpha\gamma X^3}(p_i p_l g_{jk}-p_i p_k g_{jl}$$
$$+\frac{S}{\alpha\gamma X^3}(g_{ik}p_j p_l-g_{il}p_j p_k), \tag{7, b}$$

$$\bar{R}_{ij}=\frac{g_{ij}}{X}\left\{(n-1)\frac{U}{\alpha\gamma}+\frac{Q}{\alpha\gamma^2}\right\}-\frac{p_i p_j}{X^2}\left\{(n-1)\frac{S}{\alpha^2\gamma}+\frac{Q}{\alpha\gamma^2}\right\}, \tag{8, a}$$

$$\bar{R}_{ij}=\bar{g}_{ij}\{(n-1)U\gamma+Q\}\frac{1}{\alpha^2\gamma^2}+p_i p_j\frac{(n-2)Q}{\alpha^2\gamma X^2}, \tag{8, b}$$

$$\bar{R} = (n-1)\,(nU\gamma + 2Q)\,\frac{1}{\alpha^2\gamma^2}, \tag{9}$$

$$X^2\bar{W}^i_{jkl} = \frac{Q}{\alpha\gamma^2}\left\{\frac{X}{n-1}\,(\delta^i_k g_{jl} - \delta^i_l g_{jk}) + p^i\,(p_l g_{jk} - p_k g_{jl}) + \frac{1}{n-1}\,(\delta^i_l p_j p_k - \delta^i_k p_j p_l)\right\}, \tag{10}$$

$$\bar{C}_{ijkl} = 0, \tag{11}$$

where,

$$\left.\begin{aligned} &\alpha + \beta = \gamma \\ &U = \alpha'^2 - \alpha\gamma \\ &Q = 2\alpha''\alpha\gamma - \alpha\alpha'\gamma' - 2\alpha'^2\gamma + \alpha\gamma^2 \\ &S = -2\alpha''\alpha\gamma + \alpha\alpha'\gamma' + \alpha\alpha'^2 - \alpha^2\gamma + \alpha'^2\gamma \end{aligned}\right\} \tag{12}$$

The vanishing of the conformal curvature tensor (11) gives us:

THEOREM I: *The Riemannian spaces, admitting the Lorentz group, can be mapped conformally on an S_n for* $n \geqslant 4$.

This theorem indicates that a transformation of co-ordinates exists such that

$$\frac{\alpha Y}{X} + \frac{\beta Z^2}{X^2} \to \bar{Y}\psi\,(\bar{X}). \tag{13}$$

Let such a transformation be given by

$$\bar{x}^i = \phi\,(X)\,x^i \tag{14}$$

Then,
$$\bar{Y} = \phi^2 Y + 4Z^2\,(\phi\phi' + \phi'^2 X). \tag{15}$$

In order that (13) be satisfied it is necessary and sufficient that

$$\frac{4\,(\phi\phi' + \phi'^2 X)}{\phi^2} = \frac{\beta}{\alpha X}. \tag{16}$$

The equation (16), being of standard form, can be integrated.

III. An n-dimensional Einstein space is one for which

$$\bar{R}_{ij} = \frac{\bar{R}}{n}\,\bar{g}_{ij}. \tag{17}$$

Substituting the values of R_{ij} and $\bar{R}$, (17) becomes

$$\bar{g}_{ij}\,(2-n)\,\frac{Q}{4\alpha^2\gamma^2} + p_i p_j\,(n-2)\,\frac{Q}{\alpha^2\gamma X^2} = 0. \tag{18}$$

The necessary and sufficient condition that the metric (3) should satisfy equations (17) is that

$$Q = 0. \tag{19}$$

Whence, $$\overline{W}^{i}_{jkl} = 0. \tag{20}$$

The vanishing of the projective curvature tensor indicates also the isotropy of the space.[4]

This gives us:

THEOREM II: *Einstein spaces, admitting the Lorentz group, are projectively flat and hence isotropic.*

In classical Riemannian geometry it has been shown by Schouten and Struik[5] that 'an Einstein space, if conformal to a flat space, is isotropic'. But in the present case, under discussion, an Einstein space, admitting the Lorentz group, is isotropic as well as conformal to a flat space. Therefore Theorem II is a consequence of Theorem I, hence the result of Schouten Struik.

Because the isotropic spaces of positive curvature are of class one[6], we shall find the condition such that Einstein spaces, admitting the Lorentz group, can be of positive curvature.

For $Q = 0$, the curvature tensor $(7, b)$ takes the following form:

$$\overline{R}_{ijkl} = -\frac{U}{a^2\gamma}(\bar{g}_{ik}\bar{g}_{jl} - \bar{g}_{il}\bar{g}_{jk}). \tag{21}$$

Putting (19) in the following form

$$U' - U\left(\frac{2a'}{a} + \frac{\gamma'}{\gamma}\right) = 0, \tag{22}$$

it follows on its integration that

$$\frac{U}{a^2\gamma} = \text{constant} = k^2 \text{ (say)}. \tag{23}$$

In order that the Einstein space, admitting the Lorentz group, be of constant positive curvature.

$$\left.\begin{aligned} -\frac{U}{a^2\gamma} > 0 \\ \text{or, } a\gamma - a'^2 > 0 \end{aligned}\right\} \tag{24}$$

Because of the physical interest, as will be shown in Sec. IV, we have a result for the most interesting case $n = 4$.

It is possible to represent a natural gravitational field in flat spaces of five dimensions, if and only if $a\gamma > a'^2$.

If we take

$$\overline{R} \equiv (n-1)\frac{1}{a^2\gamma^2}(nU\gamma + 2Q) = 0, \tag{25}$$

equations (17) become

$$\bar{g}_{ij}\{(n-1)\,U\gamma+Q\}\frac{1}{a^2\gamma^2}+\frac{(n-2)\,Q}{a^2\gamma X^2}p_ip_j=0. \tag{26}$$

Now, the necessary and sufficient condition that the metric (3) should satisfy equations (17) is that

$$\left.\begin{aligned}&(i)\ Q=0,\\&(ii)\ (n-1)\,U\gamma+Q=0.\end{aligned}\right\} \tag{27}$$

The equations (25, 27) are compatible and the common solution is given by

$$U\equiv a'^2-a\gamma=0, \tag{28}$$

which equivalent of a condition due to Kosambi.[3]

Equation (28) mkes $\bar{R}^i{}_{jkl}\equiv 0$, for in (7, *a*) Q and S can be put in the form of U and its derivative with respect to *log X*. Therefcre We have

THEOREM III: *Einstein spaces, admitting the Lorentz group, are flat, if and only if* $\bar{R}=0$.

Further integration of (28) is not possible unless we assign definite values to γ.

IV. The results, obtained in the previous sections, hold good also for $n=4$. Therefore, in the following pages we shall consider their physical aspects.

A fundamental need in Milne's theory of the expanding universe is that $\dot{x}^i=c\,x^i$ be a solution of equations (6), which leads to the condition that

$$\left.\begin{aligned}&A+B=2C+1^2\\&i.e.,\quad \gamma=\text{constant}\neq 0.\end{aligned}\right\} \tag{29}$$

Now, the equations (23, 28) can be integrated; their solutions being respectively

$$a=\tfrac{1}{2}m^kX^{2k}+\frac{1}{8k^4m^kX^{2k}}-\frac{1}{2k^2}, \tag{30}$$

where m, k^2 are constants of integration and $\gamma=4b^2$.

$$a=(a+b\log X)^2, \tag{31}$$

where a is constant of integration and $\gamma=4b^2$.

So far our investigation was limited to pure geometrical considerations without any application of the Einstein-field equations.

$$\bar{R}_{ij}-\tfrac{1}{2}\bar{R}\bar{g}_{ij}=-8\pi\bar{T}_{ij}, \tag{32}$$

when matter is present in the space. Equations (32) reduce to $\bar{R}_{ij}=0$ when the space is empty and this case, which corresponds to Schwarzscheld's

classical treatment, has been discussed in Sec. III. It is to be noted that the Schwarzscheld values of g_{ij} for empty space do not make the space flat, except at a very great distance from the centre of mass, but in the present case the vanishing of $\bar{R}_{ij}$ along with $\bar{R}=0$ gives a flat space (Theorem III).

Substituting the values of $\bar{R}_{ij}$, R into (32) we get the field-equations as follows:

$$\bar{g}_{ij}\,(-4\,\alpha''\alpha\gamma+\alpha'^2\gamma+2\alpha\alpha'\gamma'+\alpha\gamma^2)\,\frac{1}{\alpha^2\gamma^2}$$

$$+\frac{p_ip_j}{X^2}\cdot\frac{2}{\alpha^2\gamma}\,(2\,\alpha''\alpha\gamma-\alpha\alpha'\gamma'-2\alpha'^2\gamma+\alpha\gamma^2)=-8\,\pi\,\bar{T}_{ij}. \quad (33)$$

But
$$\bar{T}_{ij}=\bar{\epsilon}\bar{\lambda}_i\bar{\lambda}_j-p\,\bar{g}_{ij}^{6} \quad (34)$$

$$=\bar{\epsilon}\,\dot{x}_i\dot{x}_j\,M-p\bar{g}_{ij}^{2}$$

where,
$$M=\frac{\left\{\frac{\alpha^2}{X^2}+\frac{2\,\alpha\,(\gamma-\alpha)\,Z}{X^3}\sqrt{\frac{X}{Y}}+\frac{(\gamma-\alpha)^2\,Z^2}{X^3Y}\right\}}{\frac{\alpha Y}{X}+(\gamma-\alpha)\,\frac{Z^2}{X^2}}. \quad (35)$$

$$\therefore\ p=\frac{1}{8\,\pi\,\alpha^2\gamma^2}(-4\,\alpha''\alpha\,\gamma+2\,\alpha\,\alpha'\gamma'+\alpha'^2\,\gamma+\alpha\,\gamma^2)$$

$$\bar{\epsilon}=-\frac{1}{4\pi\alpha^2\gamma XY}\,(2\,\alpha''\alpha\gamma-\alpha\alpha'\gamma'-2\alpha'^2\,\gamma+\alpha\gamma^2),$$

for
$$p_ip_j=\dot{x}_i\dot{x}_j\,\frac{X^2}{Y}. \quad (36)$$

If $\bar{\epsilon}=0$, $p=\dfrac{3}{8\,\pi\,\alpha^2\gamma}\,(\alpha\,\gamma-\alpha'^2)$

Therefore, if density is zero, pressure is +ve, zero, −ve, according as

$$\alpha\,\gamma\ \begin{matrix}>\\=\\<\end{matrix}\ \alpha'^2 \quad (37)$$

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STUDIES IN THE FRIEDEL-CRAFTS REACTION

Part V. The Effect of Polar Substituents on the Reactivity of Para-substituted Phenyl Succinic Anhydrides with Simple Aromatic Hydrocarbons

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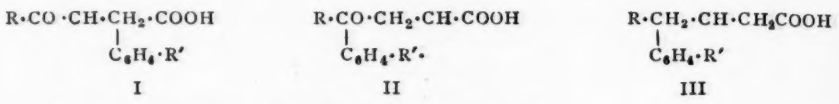
In the preceding communication,[1] evidence has been given to show that (*a*) the strong electron-donating character of the substituents, in the as-disubstituted succinic acids, is responsible for the total absence of isomerism, in condensations with simple aromatic hydrocarbons; (*b*) the tautomeric character of the phenyl group is the key-note for the appearance of isomerism in the condensation of phenyl succinic anhydride with simple aromatic hydrocarbons; (*c*) the presence of the solvent (Nitrobenzene), somehow, favours the formation of the α-β-substituted isomeride in preference to the β-β-substituted form, in the above phenyl succinic anhydride condensations; (*d*) the presence of the solvent (Nitrobenzene), somehow, inhibits the normal course of the reaction.

In the light of the above observations, it is obvious that if the electron-attracting or the electron-repelling character of the phenyl group is strengthened by the introduction of positive or negative poles, as para-substituents in phenyl succinic acid, our surmise, that an increase in the proportion of β-β-substituted isomeride to that of the α-β-substituted form, corresponding to the electron-attracting capacity of the positive pole, would take place in the first case, and a decrease in the proportion of the same isomeride, corresponding to the electron-donating capacity of the negative poles, would take place in the other case, may not be untrue.

The present investigation was undertaken, with a view, to gather as much experimental evidence as possible to lend support to our view-point. At the outset, we repeated the condensation of phenyl succinic anhydride with benzene in presence of nitrobenzene, as we considered it rather anomalous, that whereas, the anhydride condenses with toluene in presence of

nitrobenzene, and yields both the isomerides (*loc. cit.*), it does not condense with benzene under identical conditions.[2] We were able to isolate, both the isomerides in the pure state in the proportion of about 11 : 89, largely in favour of α-phenyl-β-benzoyl propionic acid (II, where $R = C_6H_5$ and $R' = H$).



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(Where $R = C_6H_5$ or C_7H_7 and $R' = H$, NO_2, $CH_3 \cdot O$ or Cl)

The isomer m.p. 154° C., gave the Piperonal and Pyrylium salt reactions, which further characterised its structure as α-phenyl-β-benzoyl propionic acid. Then we repeated the condensations of phenyl succinic anhydride with benzene, in absence of nitrobenzene (*loc. cit.*), and with toluene, with and without the solvent (*loc. cit.*) to get a more exact estimate of the mutual quantitative relationships of the two isomerides.

The work was extended to the condensation of (1) *p*-nitrophenyl and *p*-methoxyphenyl succinic anhydrides with benzene and toluene with and without the solvent (Nitrobenzene) and (2) *p*-chloro-phenyl succinic anhydride with benzene, under similar conditions. The experimental results obtained have been given under Tables I and II.

TABLE I

In the Absence of the Solvent (Nitrobenzene)

Substituent group in succinic acid	Condensed aromatic hydrocarbon	α–β-isomeride		β–β-isomeride	
		M.P. °C	%	M.P. °C	%
C_6H_5	C_6H_6	154	48	168	52
p-$NO_2 \cdot C_6H_4$ ..	,,	167	45	185	55
p-$CH_3 \cdot OC_6H_4$ ..	,,	158	Preponderates	..	..
p-ClC_6H_4	,,	146	46	166	54
C_6H_5	C_7H_8	150	23	154	77
p-$NO_2C_6H_4$	,,	173	20	178	80
p-$CH_3 \cdot OC_6H_4$ ..	,,	147	82	158	18

TABLE II

In the Presence of the Solvent (Nitrobenzene)

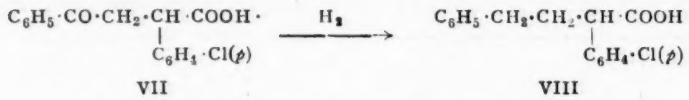
Substituent group in succinic acid	Condensed aromatic hydrocarbon	α–β-isomeride		β–β-isomeride	
		M.P. °C	%	M.P. °C	%
C_6H_5	C_6H_6	154	89	168	11
p-$NO_2 \cdot C_6H_4$ ..	,,	167	5	185	95
p-$CH_3 \cdot O \cdot C_6H_4$ ..	,,	146	Preponderates	....	.....
p-Cl C_6H_4	,,	....	.....	166	Preponderates
C_6H_5	C_7H_8	150	83	154	17
p-$NO_2 \cdot C_6H_4$ ..	,,	173	33	178	67
p-$CH_3 \cdot O.C_6H_4$ ..	,,	147	Preponderates	....	.....

The α-β form of the keto-acids always gave the characteristic pyrylium salt reaction, with salicyl aldehyde in presence of hydrogen chloride, showing the presence of $-CH_2.C=O$ grouping.[3] It also gave with piperonal, a pale yellow gum, invariably accompanied with piperonylic acid. The β-β form, on the other hand, responded to neither tests indicating the absence of the unsubstituted methylene grouping.

We were able to effect the rational synthesis of α-*p*-methoxyphenyl-β-benzoylpropionic acid (VI) from *p*-methoxy-chalkone (IV) and potassium cyanide according to the method of Lapworth and Hann.[4]

We were also able to reduce β-phenyl-β-*p*-toluoyl propionic acid, m.p. 154° C. (I, where $R = C_7H_7$ and $R' = H$) and β-*p*-chlorophenyl-β-benzoyl propionic acid, m.p. 166° C. (I, where $R = C_6H_5$ and $R' = Cl$) with its isomeride by Clemmensen's method and isolate β-phenyl-Y-*p*-tolyl butyric acid (III, where $R = C_7H_7$ and $R' = H$), Y-phenyl-β-*p*-chlorophenyl butyric acid

(III, where $R = C_6H_5$ and $R' = Cl$), and Y-phenyl-α-*p*-chlorophenyl butyric acid (VII and VIII).



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Further researches in this direction are being carried on in these laboratories, and when the results of our investigations accumulate, we shall have a clearer insight as to whether our view-point, presented elsewhere, stands the rigour of the experimental tests or not. We are also busy in effecting the synthesis of the corresponding Naphthalene derivatives from the keto-acids, mentioned hitherto, in our work.

Experimental

(*A*) *Condensations with phenyl succinic anhydride.*—

Condensation of phenyl succinic anhydride with benzene in nitrobenzene solution, and isolation of β-phenyl-β-benzoyl propionic and α-phenyl-β-benzoyl propionic acids.—A solution of anhydrous aluminium chloride (10 gms.) in nitrobenzene (50 c.c.) was gradually added to a mixture of the anhydride (5 gms.) and dry benzene (15 c.c.) with constant shaking and cooling, and kept at the room temperature for 24 hours. It was decomposed with (dil.) HCl, and then steam-distilled as usual. On cooling, a gum was obtained, which on purification through 10% sodium carbonate solution, and then drying, gave, on trituration with petrolium ether, a yellowish solid, m.p. 110–20° C. (1·6 gms.). On repeated crystallisation from benzene, it finally deposited white lustrous plates m.p. 154° C. (0·32 gms.) identified as α-phenyl-β-benzoyl propionic acid. The benzene mother liquor, finally, deposited a small amount of the isomer, β-phenyl-β-benzoyl propionic acid, m.p. 168° C. (0·01 gm.). The final mother liquors were dried, and on treatment with ethyl alcohol, yielded insoluble inorganic impurities (0·5 gm.), and a further amount (0·04 gm.) of the isomer, m.p. 168° C., on concentration. The residual sticky substance with benzene-hexane, gave the neutral substance, m.p. 285° C. (0·05 gm.) and then a yellowish gum, which on repeated treatment with hot water, gave a white solid, eventually melting at 164–67° C. (0·4 gm.), identified as impure phenyl succinic acid. While the keto-acid, m.p. 154° C. gave with piperonal, a pale yellow gum, along with piperonylic acid, m.p. 226–27° C., the isomeric keto-acid, m.p. 168° C. failed to respond the test and was always recovered unchanged. The former keto-acid gave also a pyrylium derivative, a crimson red powder, readily soluble in (dil.) caustic soda solution, and not melting below 300° C.

Phenyl succinic anhydride (6 gms.) and dry benzene (18 c.c.) were condensed in presence of anhydrous aluminium chloride (10 gms.), and 0·6 gm. of the keto-acid, m.p. 154° C., 0·65 gm. of the isomer, m.p. 168° C., and 0·6 gm. of the neutral substance, m.p. 285° C. were obtained.

Then phenyl succinic anhydride (5 gms.) was condensed, as usual, with dry toluene (15 c.c.) in presence of anhydrous $AlCl_3$ (8 gms.), and 2·7 gms. of the isomer, m.p. 154° C. and 0·8 gm. of the other isomer, m.p. 150° C. were isolated. Under identical conditions the above experiment was repeated in presence of the solvent, nitrobenzene (50 c.c.), and the isolation of 0·2 gm. of the β-β-isomeride, m.p. 154° C. and 1·0 gm. of the α-β-form was effected.

(*B*) *Condensations with* p-*nitrophenyl succinic anhydride.*—

p-Nitrophenyl succinic acid was prepared by direct nitration of phenyl succinic acid with (fuming) nitric acid at 0° C., according to the method of Fischter and Walter.[5] The crude solid, m.p. 200–10° C., when repeatedly crystallised from (dil.) alcohol, yielded white shining needles, m.p. 218° C. The anhydride was obtained by heating the above acid (12 gms.), with acetic anhydride (20 c.c.) for 4 hours and distilling excess of the acetic anhydride, under reduced pressure. The crude anhydride on crystallisation from ether, gave yellowish needles, m.p. 73° C. (10 gms.).

Condensation of p-*nitrophenyl succinic anhydride with benzene and separation of* β-p-*nitrophenyl-β-benzoyl propionic and* α-p-*nitrophenyl-β-benzoyl propionic acids.*—The proportions used were redistilled dry benzene (36 c.c.), the anhydride (12 gms.) and powdered anhydrous $AlCl_3$ (16 gms.). The crude solid, m.p. 150–60° C. (8 gms.), obtained after steam-distillation, was purified through 10% sodium carbonate, and gave a solid, m.p. 160–65° C. (7·4 gms.). It was repeatedly extracted with hot benzene and finally left a residue, m.p. 170–76° C., ultimately raised to 185° C. (0·6 gm.) on recrystallisation from methyl alcohol, and then hot benzene (long white needles). It was identified as β-β-substituted isomeride.

(Found: C, 64·7; H, 4·5; N, 4·8. $C_{16}H_{13}O_5N$ requires C, 64·2; H, 4·3; N, 4·6%.)

Concentration of the benzene extract, ultimately gave (*a*) a white crystalline solid, m.p. 218° C. (0·6 gm.) identified as the unchanged *p*-nitrophenyl succinic acid and (*b*) a white solid (small shining cubes), m.p. 167° C. (0·5 gm.) identified as α-β-substituted form, which gave the characteristic pyrylium and piperonylidene salt reactions.

(Found: C, 64·4; H, 4·8; N, 5·0. $C_{16}H_{13}O_5N$ requires C, 64·2; H, 4·3; N, 4·6%.)

On further concentration, the benzene mother liquor gave a solid, m.p. 120–30° C. (0·3 gms.), which foiled all attempts to resolve it into its components. Finally a brown sticky neutral substance (5 gms.) was left behind, which could not be solidified.

Condensation of p-*nitrophenyl succinic anhydride with benzene in nitrobenzene solution.*—The anhydride (10 gms.) and dry benzene (30 c.c.) were condensed as usual, in presence of a solution of anhydrous $AlCl_3$ (12 gms.) in nitrobenzene (50 c.c.). The solid obtained, on purification through sodium carbonate solution, melted at 170–85° C. (5·4 gms.), and from benzene-petrol, gave a white crystalline substance, m.p. 182–85° C. When re-crystallised from methyl alcohol, it gave small colourless needles, m.p. 185° C. (1·0 gm.) of β-β-substituted isomeride. The benzene extract, first deposited a crystalline substance, m.p. 218° C. (1·0 gm.), identified as the unchanged acid, and then a brownish solid, m.p. 175–80° C., which from methyl alcohol, yielded a further amount of the isomer, m.p. 185° C. (1·0 gm.). Further concentration of the benzene mother liquor, gave a solid, m.p. 150–60° C., which on recrystallisation from hot hexane, yielded white lustrous cubes, m.p. 167° C (0·1 gm.), depressed to 150–52° C. by admixture with the isomeride, m.p. 185° C. Finally, the benzene mother liquor gave a neutral brown sticky mass (2·6 gms.), which could not be obtained in the solid form.

Condensation of p-*nitrophenyl succinic anhydride with toluene and separation of* β-p-*nitrophenyl*-β-p-*toluoyl propionic and* α-p-*nitrophenyl*-β-p-*toluoyl propionic acids.*—The proportions used were, dry toluene (18 c.c.), the anhydride (6 gms.) and anhydrous $AlCl_3$ (8 gms.). The crude solid, on purification through 10% Na CO_3 yielded a brownish solid, m.p. 120–30° C. (4·8 gms.). Treatment with hot benzene-petrol left a residue, m.p. 160–70° C., which on recrystallisation from methyl alcohol, gave small shining needles, m.p. 178° C. (1·0 gm.) depressed at 160° C. by admixture with pure *p*-nitrophenyl succinic acid.

(Found: C, 65·6; H, 4·9; N, 4·5. $C_{17}H_{15}O_5N$ requires C, 65·2; H, 4·7; N, 4·4%.)

The benzene extract, on concentration, deposited first, the unchanged [illegible] m.p. 218° C. (0·54 gm.), then several fractions ranging from 155–70° [illegible] finally a pale yellow gum (neutral), which could not be solidified (2·0 gms.). The fractions (*a*) on repeated crystallisation from benzene, yielded small colourless cubes, m.p. 173° C. (0·3 gms.) depressed to 155–60° C. with the isomer 178° C. and which formed both the pyrylium salt and the piperonal derivatives.

(Found: C, 65·4; H, 4·8; N, 4·7. $C_{17}H_{15}O_5N$ requires C, 65·2; H, 4·7; N, 4·4%.)

The benzene mother liquor, finally, gave on concentration, a mixture, m.p. 120–30° C. (0·6 gm.), from which, through piperonal condensation, 0·2 gm. of the keto-acid m.p. 178° C. was recovered.

Condensation of p-nitrophenyl succinic anhydride with toluene in nitrobenzene solution.—The anhydride (10 gms.) and dry toluene (30 c.c.) were condensed as usual, in presence of a solution of anhydrous aluminium chloride (12 gms.) in nitrobenzene (50 c.c.). The crude product, on purification through sodium carbonate solution, yielded a brownish solid, m.p. 150–60° C. (6 gms.). On trituration with warm benzene-petrol, a white solid, m.p. 162–69° C. was left, which on several crystallisations from hot benzene, deposited a fraction, m.p. 170–75° C. From methyl alcohol it yielded small shining needles, m.p. 178° C. (1·0 gm.), identified as β-β-substituted isomeride. The benzene mother liquor, on slow concentration, gave first, the unchanged acid, m.p. 218° C. (0·1 gm.), and then small lustrous cubes, m.p. 173° C. (0·5 gm.) identified as the α-β-form. On further concentration, it gave (3·0 gms.) of a pale yellow gum (neutral), which could not be resolved into solid state.

(*C*) *Condensations with* p-*methoxyphenyl succinic anhydride.*—*p*-Methoxyphenyl succinic acid was prepared from *p*-methoxybenzylidene cyanacetate and potassium cyanide according to the method of Lapworth and Macrae,[6] and melted at 204° C. The anhydride prepared as usual, crystallised in small needles, m.p. 93° C.

Condensation of p-*methoxyphenyl succinic anhydride with benzene.*—The anhydride (5 gms.) and dry benzene (20 c.c.) were condensed as usual, in presence of anhydrous $AlCl_3$ (10 gms.). A brown gummy mass (4·5 gms.) was obtained, which after purification through 5% sodium bicarbonate was dissolved in hot benzene and on cooling yielded white needles, m.p. 158° C. (1·07 gms.).

(Found: C, 71·4; H, 5·8. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%.)

The benzene mother liquor, on further concentration yielded a gum (3·3 gms.), which was dissolved in alcohol and refluxed for 6 hours with an alcoholic solution of sodium acetate and semicarbazide hydrochloride. On dilution with water, a solid m.p. 170–220° C. separated out, which on fractional crystallisation through benzene yielded (*a*) a semicarbazone, m.p. 248° C. (1·2 gms.), identified as the derivative of α-β-isomer, by admixture with the pure specimen; (*b*) a neutral substance, m.p. above 290° C. (0·3 gm.);

and (*c*) a gum (1·5 gms.) which could not be resolved into its components. The original acid mother liquor, on concentration, yielded *p*-methoxyphenyl succinic acid (0·5 g.m).

Condensation of p-*methoxyphenyl succinic anhydride with benzene in nitrobenzene solution.*—The anhydride (5 gms.) and dry benzene (20 c.c.) were condensed as usual, in presence of anhydrous aluminium chloride (10 gms.) in nitrobenzene (40 c.c.), and the excess of the solvent and benzene steam-distilled. The contents on cooling gave (*a*) a clear supernatant liquid, which on concentration, yielded the unchanged *p*-methoxy-phenyl succinic acid (0·5 gm.) and (*b*) a gum which was taken up in ether, and extracted with 5% Na_2CO_3. On acidification, a gum was obtained which was dried (4 gms.) and treated with semicarbazide hydrochloride as usual. It yielded first (*a*) a neutral organic substance unmelted below 280° C. (0·7 gm.), and (*b*) yellowish long needles, m.p. 248° C. (1·6 gms.), identified as the semicarbazone of the α-β-isomeride, m.p. 158° C.

Piperonal as well as pyrylium salt reactions with the above keto-acid, gave in the first case, a pale yellow gum along with piperonyllic acid, and in the second case, a scarlet red powder, readily soluble in caustic soda solution, and not melting below 300° C.

Synthesis of α-p-*methoxyphenyl-β-benzoyl propionic acid.*—Potassium cyanide (1·5 gms.) dissolved in water (5 c.c.) was gradually added to a solution of *p*-methoxy chalkone (2 gms.) in alcohol (40 c.c.). Glacial acetic acid (1 c.c.) was then added and the mixture kept at the room temperature overnight. When the solvent was distilled off, colourless leaflets of the nitrile, m.p. 121° C. separated out. It was dissolved in 5 times its weight of concentrated sulphuric acid, and then water was added in drops till a faint but permanent turbidity was produced. The mixture was refluxed on the sand-bath, for four hours when a gum separated out. It was purified through 5% sodium carbonate, when a solid, m.p. 153° C. was obtained which on recrystallisation, through alcohol, yielded colourless needles, m.p. 158° C. Its m.p. was not depressed by admixture with the pure α-β-isomeride.

Condensation of p-*methoxyphenyl succinic anhydride with toluene.*—The proportions used were—the anhydride (5 gms.), toluene (20 c.c.) and $AlCl_3$ (10 gms.). The crude acid, on purification through sodium bicarbonate, yielded a brownish semi-solid mass (5 gms.), which when dried in vacuum, and crystallised from alcohol deposited a solid, m.p. 120–30° C. On fractional crystallisation through benzene, white needles, m.p. 147° C. (1·6 gms.) were obtained. With piperonal it gave a yellowish gum with piperonyllic

acid, and the original keto-acid was never recovered. In the pyrylium salt reaction, it gave a scarlet red solid, readily soluble in caustic soda, but unmelted below 300° C.

(Found: C, 72·8; H, 6·2. $C_{18}H_{18}O_4$ requires C, 72·5%; H, 6·0%.)

The benzene mother liquors were dried and then mixed with the alcoholic mother liquor, which on further dilution, yielded first the acid, m.p. 147° C. (0·6 gm.) and then a gum (*a*). The supernatant liquid, on concentration, yielded a solid, m.p. 153° C., which when recrystallised through benene, gave a colourless crystalline solid, m.p. 158° C. (0·6 gm.). It depressed the melting point of the keto-acid (α-β-form m.p. 147° C.) to 130° C. and failed to respond both the piperonal and pyrylium salt reactions.

(Found: C, 72·3; H, 6·2. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·0%.)

The gum (*a*) (1·7 gms.), which defied all our attempts to break up, was then treated with semicarbazide hydrochloride, and on dilution with water, yielded a solid (*b*) which when recrystallised from hot alcohol gave colourless cubes, m.p. 168° C. (0·4 gm.) (*c*) a neutral organic substance, unmelted below 280° C. (0·2 gm.) and then (*d*) a gum (1·0 gm.) which could not be crystallised out. The original mother liquor (acidic), on concentration, yielded the unchanged *p*-methoxy-phenyl succinic acid (0·5 gm.).

Condensation of p-*methoxyphenyl succinic anhydride with toluene in nitrobenzene solution.*—5 gms. of the anhydride, 20 c.c. of dry toluene and 10 gms. of aluminium chloride anhydrous in 40 c.c. of nitrobenzene were used. The crude acid was taken up in ether, and extracted with 5% sodium carbonate solution. On acidification, a solid (4·0 gms.), was obtained which on fractional crystallisation through alcohol, gave white needles m.p. 147° C. (2·1 gms.) and a gum (1·9 gms.), which on treatment with semicarbazide hydrochloride and subsequent dilution with water, gave a neutral substance, not melting below 280° C. (0·5 gm.) and then a gum (1·3 gms.), which could not be resolved into its components. The original mother liquor (acidic), on concentration, yielded the unchanged *p*-methoxy-phenyl succinic acid (0·6 gm.).

(*D*) *Condensations with* p-*chlorophenyl succinic anhydride.*—

p-*Chlorophenyl succinic acid* was prepared from *p*-chlorobenzylidene cyanacetate and potassium cyanide according to the method of Lapworth and Macrae.[6]

p-Chlorobenzylidene cyanacetate was obtained by first preparing *p*-chlorotoluene, converting it into *p*-chlorobenzaldehyde and then condensing the latter, with cyanacetic ester in presence of piperidine. The nitrile, after

purification, was condensed with potassium cyanide and the product or subsequent hydrolysis, gave the crude acid, m.p. 195–97° C. On purification through 10% sodium carbonate, it gave a yellowish white solid, m.p. 200–01° C. which on recrystalisation from ethylacetate, yielded colourless cubes of *p*-chlorophenyl succinic acid, m.p. 205° C., insoluble in benzene and cold water, and soluble in hot water and ethylacetate.

(Found: C, 52·3; H, 3·6; Cl, 15·5. $C_{10}H_9O_4Cl$ requires C, 52·5; H, 3·9; Cl 15·5%.)

p-*Chlorophenyl succinic anhydride* prepared as usual, from phenyl succinic acid and acetic anhydride crystallised from hot petrolium ether into long colourless needles, m.p. 80° C.

Condensation of p-*chlorophenyl succinic anhydride with benzene and separation of* β-p-*chlorophenyl-*β-*benzoyl propionic and* α-p-*chlorophenyl-*β-*benzoyl propionic acids.*—The proportions used were, the anhydride (6 gms.), dry benzene (18 c.c.) and anhydrous aluminium chloride (8 gms.). The crude brownish mass, on purification through sodium carbonate, yielded a solid (4 gms.), m.p. 80–100° C., which on treatment with benzene, gave an insoluble residue, m.p. 120–30° C. (*a*). On crystallisation from hot benzene and then dilute methyl alcohol, the fraction, (*a*) yielded lustrous plates, m.p. 166° C. (0·6 gm.), depressed to 150° C. by admixture with the original acid.

(Found: C, 66·1; H, 4·5; Cl, 12·1. $C_{16}H_{13}O_3Cl$ requires C, 66·5; H, 4·5; Cl, 12·3%.)

The benzene mother liquor was mixed with that from the fraction (*a*), and on concentration, first deposited a fraction, m.p. 158–62° C. (*b*), and then another fraction, m.p. 138–40° C. (*c*). The fraction (*b*) yielded the keto-acid, m.p. 166° C. (0·1 gm.), and a fraction (*c*) gave on similar treatment small shining needles, m.p. 146° C. (0·6 gm.) depressed to 127° C. by mixing with the isomer, m.p. 166° C. and to 130° C. with the original acid. It also gave the characteristic pyrylium and piperonylidene salt reactions.

(Found: C, 66·1; H, 4·5; Cl, 12·0. $C_{16}H_{13}O_3Cl$ requires C, 66·5; H, 4·5; Cl, 12·3%.)

The final mother liquor, on concentration, gave a pale yellow gum (2·5 gms.), a neutral substance, which could not be obtained in the solid form.

Condensation of p-*chlorophenyl succinic anhydride with benzene in nitrobenzene solution.*—The proportions used were, the anhydride (6 gms.), dry

benzene (18 c.c.) and anhydrous aluminium chloride (10 gms.) in nitrobenzene (50 c.c.). The contents of the flask after steam distillation, deposited a black sticky mass (*a*), and shining needles, m.p. 205° C. (1·5 gms.) identified as the unchanged acid. The crude product (*a*), on purification through 10% sodium carbonate solution, yielded a sticky mass, m.p. 80–100° C., which when triturated with hexane, deposited a brownish solid, m.p. 120–60°C. On several crystallisations from (dilute) ethyl alcohol, it yielded a very small amount of the keto-acid, m.p. 166° C. (0·1 gm.) and the unchanged *p*-chlorophenyl succinic acid (1·2 gms.). The final alcoholic mother liquor gave a brownish sticky mass, from which nothing definite could be obtained.

*Reduction of β-phenyl-β-*p*-toluoyl propionic acid by Clemmensen method, and isolation of* Y-p-*tolyl-β-phenyl butyric acid.*—A mixture of the keto-acid (1 gm.), zinc amalgam (10 gms.) and (con.) HCl was used in the reaction. The crude sticky mass, on purification through 10% sodium carbonate, gave a white solid, m.p. 70–75° C. Repeated crystallisation from petrolium ether gave ultimately, small needles, m.p. 104° C. (0·8 gm.).

(Found: C, 79·8; H, 7·1. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%.)

Reduction of β-p-*chlorophenyl-β-benozyl propionic acid*, was effected by Clemmensen method. The crude solid on purification through sodium carbonate yielded a solid, m.p. 83–85° C., which when recrystallised from petrolium ether, gave short colourless needles, m.p. 86° C. of Y-phenyl-*β-p*-chlorophenyl butyric acid.

(Found: C, 69·4; H, 5·4; Cl, 12·6. $C_{16}H_{15}O_2Cl$ requires C, 69·8; H, 5·4; Cl, 12·9%.)

Reduction of α-p-*chlorophenyl-β-benzoyl propionic acid*, was effected in similar way. The white solid, m.p. 140–45° C. was obtained which on recrystallisation from benzene gave lustrous needles of Y-phenyl-*α-p*-chloro phenyl butyric acid, m.p. 150° C. depressed to 120° C. by the original keto-acid.

(Found: C, 69·3; H, 5·4; Cl, 12·6. $C_{16}H_{15}O_2Cl$ requires, C, 69·8; H, 5·4; Cl, 12·9%.)

Summary

The influence of the *p*-nitrophenyl, *p*-methoxyphenyl, and *p*-chlorophenyl groups (in *p*-substituted phenyl succinic acid) compared to that of the phenyl group (in phenyl succinic acid) has been studied in condensations with simple aromatic hydrocarbons and the results have been embodied in Tables I and II.

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THE REDUCTION OF $-CH(OH)CCl_3$ GROUP ATTACHED TO A BENZO-α-PYRONE NUCLEUS

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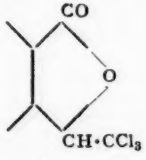
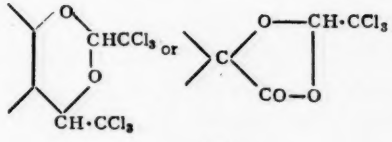
The reduction of $-CH(OH)CCl_3$ group in trichloro-methyl carbinols present as such or potentially formed during the course of reduction from trichloro-methylphthalide ring (A) or the heterocyclic ring (B) has been an interesting subject for investigation by numerous workers. Using zinc and boiling alcohol, Jocitsch[1] found that the reaction took the course thus:

$$Ph{-}CH(OH)CCl_3 \rightarrow Ph{-}CH = CCl_2.$$

The best results were obtained by reducing the acetyl derivative, using the zinc in form of its shavings. Jocitsch also studied the tertiary alcohols containing the group $\rangle C(OH)CCl_3$. According to his method of reduction, the group $-CH(OH)CCl_3$ is converted into $-CH = CCl_2$; and the group $\rangle C(OH)CCl_3$ into $\rangle C = CCl_2$.



(A)



(B)

Using zinc dust and glacial acetic acid as reducing agents, Meldrum and Alimchandani[2] observed that in several compounds investigated by them, the group $-CH(OH)CCl_3$ is reduced with the production of $-CH_2.CHCl_2$ group. In extending their study of this reduction, Meldrum and his several collaborators[3] applied it to a large number of compounds including those of the type (A) and (B) shown above. On the other hand, Wheeler and

Yelburgi[4] proved that the group $-CH(OH)CX_3$ ($X = Cl$ or Br) is reduced to $-CH = CX_2$ and not to $-CH_2 \cdot CHX_2$ in case of chloral- and bromal-amides.

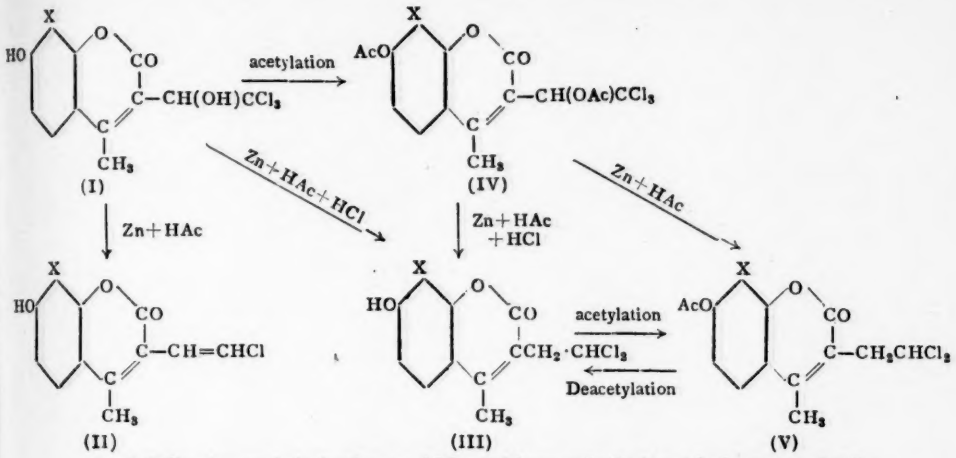
$$R \cdot CO \cdot NH \cdot CH(OH)CX_3 \rightarrow R \cdot CO \cdot NH \cdot CH = CX_2$$

Recently Dharwarkar and Alimchandani[5] have shown that in the case of some chloral-hydroxy-benzoic acid derivatives, the group $-CH(OH)CCl_3$ gets reduced to the unsaturated group $-CH = CCl_2$, and not to the saturated group $-CH_2 \cdot CHCl_2$ as erroneously postulated by Meldrum and collaborators. It is clear from the brief survey given above that in all the cases investigated hitherto, the group $-CH(OH)CCl_3$ is present either in the open-chain derivatives or is attached to an aromatic nucleus.

During the course of our studies on the effect of α-substituents in the Pechmann condensation, a number of benzo-α-pyrones (coumarins) containing $-CH(OH)CCl_3$ group in 3-position of the pyrone ring were synthesised by Kulkarni, Alimchandani and Shah.[6] Because the reduction of $-CH(OH)CCl_3$ group attached to a benzo-α-pyrone nucleus is hardly known, a study of the reduction of various 3-$CH(OH)CCl_3$- substituted coumarin derivatives synthesised by Kulkarni, Alimchandani and Shah was undertaken by the present authors, the reducing agents used being zinc dust and glacial acetic acid, (*a*) in conjunction with concentrated hydrochloric acid and (*b*) without the hydrochloric acid.

7-Hydroxy-3-(α-hydroxy-βββ-trichloro-ethyl)-4-methylcoumarin (I) on reduction by zinc dust and acetic acid gave 7-hydroxy-3-(β-chloro-vinyl)-4-methyl-coumarin (II). On carrying out the same reduction in conjunction with conc. hydrochloric acid, 7-hydroxy-3-(ββ-dichloro-ethyl)-4-methyl-coumarin (III) was obtained. Evidently, the addition of hydrochloric acid to the β-chloro-vinyl group produced by the reduction takes place with the ultimate production of the $-CH_2 \cdot CHCl_2$.

The acetyl derivative of (I), 7-acetoxy-3-(α-acetoxy-βββ-trichloro-ethyl)-4-methylcoumarin (IV) on similar reduction by zinc and acetic acid gave 7-acetoxy-3-(ββ-dichloro-ethyl)-4-methyl-coumarin (V) identical with the acetoxy derivative of (III), which is obtained directly by the reduction of (IV) in presence of conc. hydrochloric acid. The results are shown diagrammatically below : ($X = H$ in all compounds in this series)



7 : 8-Dihydroxy-3-(α-hydroxy-βββ-trichloro-ethyl)-4-methyl-coumarin (I ; X = OH) behaves exactly similarly; it gave 7 : 8-dihydroxy-3-(β-chloro-vinyl)-4-methylcoumarin (II ; X = OH) and 7 : 8-dihydroxy-3-(ββ-dichloroethyl)-4-methylcoumarin (III ; X = OH) when reduced without and with conc. hydrochloric acid respectively. The acetoxy derivative (IV ; X = OAc) on reduction by zinc and acetic acid only gave V (X = OAc) identical with the acetyl derivative of the coumarin III (X = OH), obtained directly on reduction in presence of conc. hydrochloric acid of the acetoxy derivative (IV).

The reduction of 5-hydroxy-4 : 7-dimethyl-3-(α-hydroxy-βββ-trichloro-ethyl)-coumarin also takes a similar course : on reduction by zinc and acetic acid (*a*) without conc. hydrochloric acid and (*b*) in the presence of the acid, it gave (*a*) 5-hydroxy-4 : 7-dimethyl-3-(β-chloro-vinyl)- and (*b*) -3-(ββ-dichloroethyl)-coumarin derivatives respectively.

5 : 7-Dihydroxy-3-(α-hydroxy-βββ-trichloro-ethyl)-4-methylcoumarin on reduction by zinc and acetic acid gave a product which could not be crystallised. But its acetoxy derivative was smoothly reduced by zinc and acetic acid to 5 : 7-diacetoxy-3-(ββ-dichloro-ethyl)-4-methyl coumarin, which was deacetylated to the corresponding 5 : 7-dihydroxy-derivative.

4-Methyl-3-(α-hydroxy-βββ-trichloro-ethyl)-1 :2-α-naphtha-pyrone and 4 :6 dimethyl-3-(α-hydroxy-βββ-trichloroethyl)-coumarin gave only one type of the reduction product, *viz.*, 3-(ββ-dichloroethyl), whether hydrochloric acid was used or not during the reduction as in the previous cases.

From the above results and those of the previous investigators on the reduction of –CH(OH)CCl_3 group, it is evident that the reduction does not

proceed in a uniform manner in all cases. It is highly affected by the constitutional factors. A study of the reduction products of $-CH(OH)CCl_3$ present in several coumarins described in this paper supports the above point. The following generalisation of the results described in this communication reveals some interesting points :

(*a*) On reduction with zinc and acetic acid, the group $-CH(OH)CCl_3$ in the pyrone ring is reduced to $-CH = CHCl$ group in case of hydroxycoumarins, *i.e.*, those obtained from resorcinol, pyrogallol, etc.

(*b*) The same group $-CH(OH)CCl_3$ is reduced to $-CH_2 \cdot CHCl_2$ when:

(i) the reduction is carried out in conjunction with concentrated hydrochloric acid;

(ii) the phenolic group (–OH) is absent, as in case of coumarins obtained from α-naphthol and *p*-cresol; and

(iii) the phenolic –OH group is protected by acetylation.

Experimental

(*A*) *Reduction of 7-hydroxy-3-(α-hydroxy-βββ-trichloro-ethyl)-4-methylcoumarin*:

1. Formation of 7-hydroxy-3-(β-chloro-vinyl)-4-methyl-coumarin.—This reduction was carried out by means of zinc dust and acetic acid according to the details of Kulkarni, Alimchandani and Shah.[6] The reduction product obtained melted at 254–55° (decomp.) not depressed by mixture with the sample of those authors.

2. Formation of 7-hydroxy-3-(ββ-dichloro-ethyl)-4-methylcoumarin.—(*a*) The coumarin (2 g.) was dissolved in hot glacial acetic acid (30 c.c.) and the solution mixed with conc. HCl (6–7 c.c.). Zinc dust (2 g.) was gradually added with stirring. After reaction subsided, the solution was boiled for a few minutes, filtered from the unchanged zinc and the filtrate diluted with water. The reduction product was collected and crystallised from dil. alcohol, yellowish needles, m.p. 206–07°. [Found: Cl, 26·29; $C_{12}H_{10}O_3Cl_2$ requires Cl, 26·02 per cent.]

(*b*) 7-Acetoxy-3-(α-acetoxy-βββ-trichloro-ethyl)-4-methylcoumarin was similarly reduced as above. The reduction product was found to be identical with the above product.

3. Formation of 7-acetoxy-3-(ββ-dichloro-ethyl)-4-methylcoumarin.—(*a*) The above reduction product (0·5 g.) was dissolved in acetic anhydride (7 c.c.) in presence of conc. sulphuric acid (4 drops). The clear solution was shaken for about 10–15 minutes and poured into water. The solid was collected and

crystallised from rect. spirit, rhombic plates, m.p. 101–02°. [Found: Cl, 22·9; $C_{14}H_{12}O_4Cl_2$ requires Cl, 22·54 per cent.] It does not exhibit any fluorescence.

(*b*) The above substance was also obtained directly by reducing 7-acetoxy-3-(α-acetoxy-βββ-trichloro-ethyl)-4-methylcoumarin (0·5 g.) by adding zinc dust (0·7 g.) to its acetic acid solution in the usual way, m.p. 101–02° (yield 0·3 g). The mixed melting point of this compound with the derivative obtained by (*a*) was unchanged.

4. *De-acetylation of the above acetoxy derivative.*—The acetoxy derivative (1 g.) was suspended in methyl alcohol (10 c.c.) and conc. H_2SO_4 (8 c.c.) added ; the mixture was refluxed on water-bath for an hour and a half. After cooling, it was diluted witn water and the substance obtained crystallised from acetic acid (animal charcoal), m.p. 206–07°, the mixed m.p. with 7-hydroxy-3-(ββ-dichloro-ethyl)-4-methylcoumarin obtained above remaining undepressed.

(*B*) *Reduction of* 7: 8-*dihydroxy*-3-(α-*hydroxy-βββ-trichloroethyl*)-4-*methylcoumarin*:

1. *Formation of* 7 : 8-*dihydroxy*-3-(β-*chloro-vinyl*) 4-*methylcoumarin.*—The procedure followed by Kulkarni, Alimchandani and Shah[6] was employed and the reduction carried out as usual. The reduction product crystallised from alcohol, needles, m.p. 231–32°. The mixed melting point was also undepressed.

2. *Formation of* 7 : *8-dihydroxy*-3-(*ββ-dichloro-ethyl*)-4-*methylcoumarin.*—(*a*) The coumarin (8 g.) dissolved in acetic acid (100 c.c.) and mixed with conc. HCl (30 c.c.) was slowly treated with zinc (7 g.). Vigorous reaction took place. When the reaction subsided, the unchanged zinc was removed and the filtrate diluted with water. The product crystallised from acetic acid and then from benzene, hexagonal prisms, m.p. 195–96°, yield 5. g. [Found: Cl, 24·73; $C_{12}H_{10}O_4Cl_2$ requires 24·52 per cent.]

(*b*) The same reduction product was obtained by carrying out the reduction of 7 : 8-di-acetoxy-3-(α-acetoxy-βββ-trichloro-ethyl)-4-methylcoumarin in presence of conc. HCl as before.

The *acetyl* derivative prepared by acetic anhydride-pyridine method crystallised from alcohol, needles, m.p. 163–164°. [Found: Cl, 18·88; $C_{16}H_{14}O_6Cl_2$ requires Cl, 19·0 per cent.]

The same acetyl derivative was obtained by the reduction of 7 : 8-di-acetoxy-3-(α-acetoxy-βββ-trichloro-ethyl)-4-methylcoumarin using zinc dust and acetic acid as usual.

The de-acetylation of the substance by conc. sulphuric acid in methyl alcoholic solution gave the corresponding 7 : 8-di-hydroxy-coumarin identical in all respects with the same substance described already.

(*C*) *Reduction of* 5-*hydroxy*-4 : 7-*dimethyl*-3-(α-*hydroxy*-βββ-*trichloro-ethyl*)-*coumarin*:

1. Formation of 5-*hydroxy*-4 : 7-*dimethyl*-3-(β-*chloro-vinyl*)-*coumarin*.—The coumarin (1 g.) was suspended in hot acetic acid (15 c.c.) and zinc dust (1 g.) added gradually as in previous cases. As the reaction proceeded, the substance went into solution. The reduction product was isolated as before and crystallised from dil. alcohol, diamond-shaped crystals, m.p. 251–52°. [Found: Cl, 14·24; $C_{13}H_{11}O_3Cl$ requires Cl, 14·16 per cent.]

The *acetyl* derivative obtained by acetic anhydride-pyridine method (2½ hours refluxing on water-bath) crystallised from alcohol in needles, m.p. 148–49°. [Found: Cl, 11·92; $C_{15}H_{13}O_4Cl$ requires Cl, 12·12 per cent.]

2. Formation of 5-*hydroxy*-4 : 7-*dimethyl*-3-(ββ-*di-chloro-ethyl*)-*coumarin*.—The above reduction was carried out in presence of conc. HCl (4 c.c.) and the reduction product isolated as before ; first crystallised from alcohol and then from ethyl acetate, needles, m.p. 242°. [Found: Cl, 24·83; $C_{13}H_{12}O_3Cl_2$ requires Cl, 24·69 per cent.]

The *acetyl* derivative prepared as before crystallised from dilute alcohol, rectangular plates, m.p. 157°. [Found: Cl, 21·30; $C_{15}H_{14}O_4Cl_2$ requires Cl, 21·54 per cent.]

(*D*) *Formation of* 5 : 7-*di-acetoxy*-3-(ββ-*dichloro-ethyl*)-4-*methylcoumarin*:

5 : 7-Diacetoxy-3-(α-acetoxy-βββ-trichloro-ethyl)-4-methylcoumarin (2 g.) was reduced by means of zinc dust (2·5 g.) and acetic acid (25 c.c.) as in previous cases. The product crystallised from dil. alcohol, rectangular rods, m.p. 121–22°. [Found: Cl, 18·91; $C_{16}H_{14}O_6Cl_2$ requires Cl, 19·0 per cent.]

De-acetylation of the above 5 : 7-*diacetoxy-coumarin derivative*.—The de-acetylation was effected by sulphuric acid (7 c.c.) in methyl alcohol solution (1 g. in 10 c.c.) by refluxing for 1½ hours on water-bath. The solution was diluted with water and the substance obtained crystallised from dil. alcohol, thin flakes, m.p. 246–47°. [Found: Cl, 24·67; $C_{12}H_{10}O_4Cl_2$ requires Cl, 24·52 per cent.]

(*E*) *Formation of* 4-*methyl*-3-(ββ-*di-chloroethyl*)-1 : 2-α-*naphtha-pyrone*:

4-Methyl-3-(α-hydroxy-βββ-trichloro-ethyl)-1 : 2-α-naphtha-pyrone (2·5 g.) was reduced by zinc (2·5 g.) in its acetic acid solution (30 c.c.) and the product isolated as before. It first crystallised from dichlorobenzene and

then from xylene, m.p. 221–22° (yield, 1·5 g.). [Found: Cl, 22·71; $C_{16}H_{12}O_2Cl_2$ requires Cl, 23·09 per cent.]

The same product was obtained by carrying out the reduction in presence of conc. HCl (4 c.c. for 1 g. of the coumarin).

Formation of 4: 6-*dimethyl*-3-(*ββ-dichloro-ethyl*)-*coumarin.*—4: 6-Dimethyl -3-(α-hydroxy-βββ-trichloro-ethyl)-coumarin (1 g.) was reduced as before (zinc 1 g. + acetic acid 15 c.c.). The product crystallised from alcohol in rectangular plates, m.p. 206–07°. [Found: Cl, 25·84; $C_{13}H_{12}O_2Cl_2$ requires Cl, 26·16 per cent.]

A better yield is obtained if the above reduction is carried out in conjunction with conc. HCl (4 c.c. for 1 g. of the coumarin).

We thank Prof. M. S. Shah and Prof. R. L. Alimchandani for their interest and facilities for the work. We are grateful to Dr. R. C. Shah for his useful suggestions and interest in the investigation.

Summary

The reduction of $-CH(OH)CCl_3$ group attached to a benzo-α-pyrone nucleus has been studied for the first time, the reducing agents used being zinc dust and glacial acetic acid either in conjunction with conc. HCl or without it. It is found that the course of the reduction is highly affected by the constitutional factors. The following generalisation is made in this connection:

(*a*) on reduction with zinc and acetic acid, the group $-CH(OH)CCl_3$ in the pyrone ring is reduced to $-CH=CHCl$ group in case of hydroxy-coumarins; (*b*) the same group $-CH(OH)CCl_3$ is reduced to $-CH_2CHCl_2$ group if (i) the reduction is carried out in conjunction with conc. HCl; (ii) the phenolic group –OH is either absent or is protected by acetylation.

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PYRONINE DYESTUFFS DERIVED FROM SUCCINIC ACID

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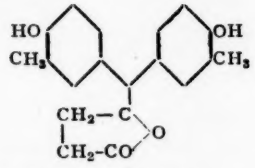
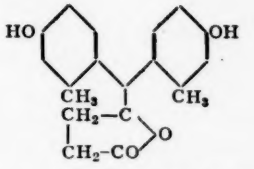
Resorcinolsuccinein or what is commonly known as succinyl-fluorescein has been known in an impure condition ever since Baeyer[1] prepared ordinary fluorescein or resorcinol-phthalein by the action of phthalic anhydride on resorcinol. In 1923 Biggs and Pope[2] obtained resorcinol-succinein in a pure condition and in the following year Dutt and Thorpe[3] were successful in getting it in a finely crystalline form. The same authors also prepared succinyl-rhodamine or *m*-dimethylamidophenol-succinein hydrochloride in glistening needles, having properties almost identical with ordinary rhodamine or *m*-dimethylamidophenol-phthalein hydrochloride. Two years later on, that is in 1926, Dutt[4] prepared phenol-succinein for the first time as colourless prisms melting at 252° C., and dissolving in dilute sodium hydroxide with intense crimson colour, just like ordinary phenol-phthalein. A large number of analogous derivatives of succinic acid were prepared by the same author by condensation of the anhydride with aromatic phenols and amino compounds, and the results although incorporated in the thesis for the degree of Doctorate of Science of the London University, were not subsequently published in consideration of the fact, that, as the most important compounds of the series had already been published, the analogous compounds were not of sufficient importance to deserve publication by themselves. But in view of a recent paper by Dass and Tewari[5] describing many of these analogous succineins and containing results which are not only highly surprising but are beyond all normal expectations, that the present author has thought it necessary and desirable to publish his own experimental results carried out in this connection in the London University nearly 16 years ago and also corroborated by recent experiments carried out in India. The results have been tabulated at the end of the experimental portion of the paper, and for the sake of comparison have been grouped against the corresponding results of Dass and Tewari and also against known data regarding the corresponding phthaleins.

The most remarkable feature about the work of Dass and Tewari mentioned above with regard to the succineins is that they have described the

greater majority of them as a series of *black powders*, whereas the present author could only isolate them as colourless crystalline substances, just like the corresponding phthaleins. *O*-cresol-succinein and *m*-cresol-succinein have been given the molecular formula of $C_{18}H_{16}O_3$ by Dass and Tewari which is definitely wrong, since undoubtedly they possess the following molecular structures :

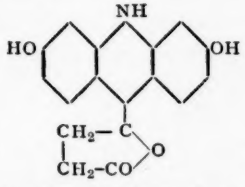


o-Cresol-succinein



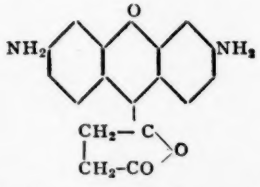
m-Cresol-succinein

and therefore the molecular formula $C_{18}H_{18}O_4$. Similar is the case with the compound, *m*-amidophenol-succinein, which they have described as a violet powder soluble in caustic soda and insoluble in acids. The formula that Dass and Tewari have given to the substance, that is $C_{16}H_{14}O_3N_2$, is apparently wrong, as it is undoubtedly phenolic in character and therefore possesses the molecular structure given below:—



m-Amidophenol-succinein

which corresponds to the formula $C_{16}H_{13}O_4N$. Had the authors determined the nitrogen content of their compound, they would have easily found out their mistake. The structural formula assumed by Dass and Tewari for their substance, that is:



is incompatible with the properties of the compound described by themselves since with the above formula, it is not possible even by a stretch of imagination

to visualise how the substance could dissolve in caustic soda and get precipitated by acids. On the contrary one would easily think that with such a formula which is that of a true rhodamine, this substance would, like a rhodamine, get easily dissolved in acids and precipitated by alkalies. Apparently the authors are not aware of the fact that *m*-amidophenol condenses with diabasic acid anhydrides in a different way to that of *m*-dimethyl amidophenol, and the two condensation products have different properties. This has already been clearly shown by Dutt[6] as early as 1923.

Experimental

O-*Cresol-succinein.*—This was prepared by heating *o*-cresol with succinic anhydride in presence of stannic chloride in the same way as phenol-succinein (Dutt[4]). Two products were simultaneously formed, one being *o*-cresol-succinein (major fraction) and the other *o*-cresol-succinein-anhydride, and they were separated from each other by the action of caustic soda in which the former only is soluble.

O-Cresol succinein crystallises from alcohol in colourless prisms melting at 264° C. and dissolving in alkalies with an intense crimson colour. (Found : C = 72·3; H = 6·3. $C_{18}H_{18}O_4$ requires C = 72·5; H = 6·0%.)

O-Cresol-succinein-anhydride crystallises from glacial acetic acid in colourless glistening needles melting at 178–79° C. and is insoluble in alkalies or ammonia. It has properties very similar to *o*-phenol-phthalein-anhydride or fluoran first prepared by Baeyer[7] in 1892. (Found : C = 76·8; H = 5·9. $C_{18}H_{16}O_3$ requires C = 77·1; H = 5·7%.)

M-*Cresol-succinein.*—This was prepared from succinic anhydride and *m*-cresol in the same way as *o*-cresol-succinein. It crystallises from dilute alcohol in colourless glistening prisms melting at 146° C. and dissolves in dilute alkalies and ammonia with a bright pink colour. (Found: C = 72·2; H = 6·2. $C_{18}H_{18}O_4$ requires C = 72·5; H = 6·0%.)

α-*Naphthol-succinein.*—This was prepared by heating a mixture of succinic anhydride (10 g.), α-naphthol (14 g.) and chlorosulphonic acid (5 g.) at 100–110° C. for 4 hours in a stream of carbon dioxide. The melt was then poured into a litre of boiling water and the insoluble grey precipitate filtered off and repeatedly crystallised from alcohol with the addition of animal charcoal ultimately as colourless needles melting at 245° C. It dissolves in dilute alkalies and ammonia with an intense blue colour. (Found : C = 81·6; H = 4·8. $C_{24}H_{18}O_4$ requires C = 81·8; H = 4·5%.)

Quinol-succinein.—This was prepared by heating a mixture of succinic anhydride (10 g.), quinol (22 g.) and concentrated sulphuric acid (1 c.c.) at

160–170° C. for 6 hours in a current of carbon dioxide. The melt was poured into boiling water and the insoluble precipitate crystallised from dilute alcohol with the addition of animal charcoal in colourless glistening prisms melting at 258° C. It dissolves in dilute alkalies and ammonia with an intense violet colour, which however soon oxidises and becomes ultimately brownish-yellow. (Found: C = 67·3; H = 4·5. $C_{16}H_{12}O_5$ requires C = 67·6; H = 4·2%.)

Catechol-succinein.—This was prepared from catechol and succinic anhydride in the same way as catechol-citraconein (Dhar and Dutt[8]), catechol itaconein (Dhar and Dutt[9]) or catechol-β-phenylpyridine-dicarboxylein (Tewari and Dutt[10]). The substance crystallises from alcohol in colourless glistening prisms melting at 286° C. It dissolves in caustic allakies and ammonia with a transcient green colour, which rapidly becomes brown by oxidation, particularly on exposure to the air. In all these respects, catechol-succinein is perfectly analogous to catechol-phthalein first prepared by Meyer[11] in 1905. (Found: C = 67·2; H = 4·4. $C_{16}H_{12}O_5$ requires C = 67·6; H = 4·2%.)

Pyrogallol succinein.—This was prepared from pyrogallol and succinein anhydride in the same way as quinol-succinein. It crystallises from dilute alcohol in colourless glistening prisms melting at 276° C. It dissolves in dilute alkalies and ammonia with a blue colour. (Found: C = 60·4; H = 4·1. $C_{16}H_{12}O_7$ requires C = 60·7; H = 3·8%).

Phloroglucinol-succinein.—This was prepared from succinic anhydride and phloroglucinol in the same way as resorcinol succinein. It crystallises from dilute alcohol acidified with hydrochloric acid in bright orange-yellow prisms melting above 300°C. (Found: C = 60·5; H = 4·1. $C_{16}H_{12}O_7$ requires C = 60·7; H = 3·8%.)

M-*amidophenol-succinein.*—This was prepared from *m*-amidophenol and succinic anhydride in the same way as 2:2′-iminophenol-sulphamphthalein (Dutt[12]). The substance crystallises from dilute alcohol in light-brown prisms melting at 224° C. It dissolves in dilute alkalies and ammonia with a brownish yellow-colour, but without any fluorescence. The alcoholic and acetic acid solutions are brownish-yellow with moss-green fluorescence. (Found: N = 4·8; $C_{16}H_{13}O_4N$ requires N = 4·98%.)

M-*phenylenediamine-succinein.*—This was prepared from *m*-phenylenediamine hydrochloride and succinic anhydride in the same way as the corresponding camphorein (Sircar and Dutt[13]). The substance crystallised from dilute alcohol in bright yellow glistening plates melting at 242° C. It is insoluble in alkalies or ammonia, but dissolves in dilute acids with an intense orangered colour. (Found: N = 15·3; $C_{16}H_{15}O_2N_3$ requires N = 14·9%.)

TABLE I

General Properties of the Succineins

(D = prepared by Dutt. DT = prepared by Dass and Tewari
S = succinein)

Name of the compound	Appearance	M.P. (° C.)	Colour in alcohol	Colour in alkali
Phenol—S (D)	Colourless prisms	252	Colourless	Crimson
Do. (DT)	..	..	..	..
O-cresol—S (D)	Colourless prisms	264	Colourless	Crimson
Do. (DT)	Chocolate-brown powder	195 blacken, 230 melt	Chocolate-brown	Reddish-violet
M-cresol—S (D)	Colourless prisms	146	Colourless	Crimson
Do. (DT)	Light brown powder	112	Brownish-orange	Brownish-orange
α-Naphthol—S (D)	Colourless prisms	245	Colourless	Deep blue
Do. (DT)	Black powder	185	Pink-orange	Pink-orange
Resorcinol—S (D)	Brown needles	234	Yellow	Orange-yellow
Do. (DT)	..	..	..	..
Catechol—S (D)	Colourless prisms	286	Colourless	Transcient green
Do. (DT)	Black powder	Above 290	Dirty greenish-yellow	Dull green
Quinol—S (D)	Colourless prisms	258	Colourless	Transcient violet
Do. (DT)	..	..	..	..
Pyrogallol—S (D)	Colourless prisms	276	Colourless	Blue
Do. (DT)	Grey-black powder	Above 290	Deep mahogany-brown	Violet
Phloroglucinol—S (D)	Orange-yellow prisms	Above 290	Orange-yellow	Orange-red
Do. (DT)	..	..	..	..
M-amidophenol—S (D)	Light brown prism	224	Brownish-yellow	Brownish-yellow
Do. (DT)	Violet powder	198	Violet-red	Violet-red
M-dimethylamido-phenol-S (HCl) (D)	Brown needles	225–30	Bluish-red	Insoluble
Do. (DT)	..	..	..	..
M-phenylene-diamine—S (D)	Yellow plates	242	Yellow	Insoluble
Do. (DT)	Clay-coloured powder	210	..	..

TABLE II

Colour and Absorption Maxima of the Succineins

(D = prepared by Dutt. DT = prepared by Dass and Tewari.
S = Succinein. P = Phthalein)

Name of the compound	Colour in alcohol	Absorption maxima in ditto (Å)	Colour in alkali	Absorption maxima in ditto (Å)
Phenol—S (D)	Colourless	..	Crimson	5450
Do. —S (DT)	..	..	..	5450
Do. —P	Colourless	..	Crimson	5550
O-cresol—S (D)	do.	..	do.	5460
Do. —S (DT)	Chocolate-brown	4800	Reddish-violet	6250
Do. —P	Colourless	..	Crimson	5565
M-cresol—S (D)	do.	..	do.	5450
Do. —S (DT)	Brownish-orange	4000	Brownish-orange	4000
Do. —P	Colourless	..	Crimson	5555
α-naphthol—S (D)	do.	..	Deep blue	6080
Do. —S (DT)	Pink-orange	4400	Pink-orange	4850
Do. —P	Colourless	..	Deep-blue	6100
Resorcinol—S (D)	Yellow	4709	Orange	4936
Do. —S (DT)	..	5000	..	5200
Do. —P	Yellow	4800	Orange	4940
Catechol—S (D)	Colourless	..	Green	6500
Do. —S (DT)	Dirty greenish-yellow	4300	Dull green	4600
Do. —P	Colourless	..	Green	6650
Quinol—S (D)	do.	..	Violet	5810
Do. —S (DT)	..	..	..	..
Do. —P	Colourless	..	Violet	5900
Pyrogallol—S (D)	do.	..	Blue	5950
Do. —S (DT)	Deep mahogany	5970	Violet	6750
Do. —P	Colourless	..	Blue	5980

TABLE II—*Contd.*

Name of the compound	Colour in alcohol	Absorption maxima in ditto (Å)	Colour in alkali	Absorption maxima in ditto (Å)
Phloroglucinol—S (D)	Orange-yellow	4800	Orange	4920
Do. —S (DT)	..	..	..	..
Do. —P	Orange-yellow	4850	Orange	4980
M-amidophenol—S (D)	Brownish-yellow	4750	Brownish-yellow (acid)	4800 (acid)
Do. —S (DT)	Violet-red	5900	Violet-red („)	5950 („)
Do. —P	Brown	4850	Brown („)	4910 („)
M-dimethylamido-phenol—S (HCl) (D)	Bluish-red	5465	Bluish-red („)	5465 („)
Do. —S (DT)	..	..	..	..
Do. —P (HCl)	Deep pink	5550	Deep pink („)	5550 („)
M-phenylene-diamine—S (D)	Yellow	4550	Orange-red („)	5000 („)
Do. —S (DT)	..	4450	..	4750 („)

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ON THE CYANOGEN HALIDES

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I. Action of Halogens on Cyanogen Halides

No observations appear to have been recorded on the action of halogens on cyanogen halides except that of chlorine on cyanogen chloride (Wurtz, 1851; Naumann and Vogt, 1870) and bromine on cyanogen bromide in ether (Poonamarew, 1885) which polymerise them to cyanuric chloride and cyanuric bromide respectively. The object of the present investigation is to study the possible displacement reactions with the cyanogen halides.

The action of chlorine gas on cyanogen iodide and the action of bromine on cyanogen chloride were first studied. It was expected that chlorine would displace iodine from cyanogen iodide forming cyanogen chloride, but it was found that cyanogen iodide was not affected by dry chlorine. Dry cyanogen iodide, prepared by warming an intimate mixture of one part of iodine and two parts of AgCN, at about 40°, was sublimed into a narrow tube which could be heated in a water-bath. Dry chlorine was passed through the tube for nearly two hours. No immediate reaction occurred, and even after leaving for a week at room temperature (30°) the white needles of cyanogen iodide remained unchanged. The tube was then slowly heated, but no reaction occurred up to the sublimation temperature of cyanogen iodide (about 40°). It was found that cyanogen iodide could be sublimed unchanged in an atmosphere of dry chlorine.

Since chlorine does not displace iodine from cyanogen iodide, it was thought that bromine might displace chlorine from cyanogen chloride forming cyanogen bromide. This reaction, however, is not simple.

Experimental

Cyanogen chloride was produced by the action of chlorine on aqueous hydrocyanic acid (10–15%) prepared by distilling potassium ferrocyanide with dilute sulphuric acid. The aqueous HCN was placed in a series of gas washing bottles containing glass beads. The last wash bottle was connected to a U-tube of calcium chloride which was sealed to a glass spiral cooled in

ice and salt. A steady current of chlorine was then passed through the aqueous hydrocyanic acid. The cyanogen chloride formed condensed in the spiral as a colourless liquid. The liquid CNCl was then purified by passing excess of chlorine to remove any free HCN, treated with pure dry mercury to remove the excess of chlorine, and finally distilled through sodium bicarbonate and calcium chloride to remove HCl and moisture respectively (Price and Green, 1920).

The reaction between bromine and cyanogen chloride was allowed to take place in a U-tube with taps sealed at either end. The bromine was distilled over fused calcium bromide into the apparatus and then the cyanogen chloride was distilled into the same. For about 10 c.c. of liquid bromine, 8–9 c.c. of CNCl were taken. After about 12 hours the liquid mixture of bromine and cyanogen chloride solidified to short needle-shaped crystals. The reaction was allowed to continue for five days more.

After this period, the excess of bromine was removed by passing a current of dry air through the apparatus and then through strong alkali. The alkali was tested in the end and found to contain no cyanogen compound. The solid residue was then treated with pure dry chloroform, in which almost the whole of it dissolved. The solution was filtered and the chloroform distilled off, when a crystalline product was formed. This was re-dissolved in chloroform and crystallised, when shining plates were obtained. Re-crystallisation from petroleum ether (60–80°) gave feather-shaped crystals.

This substance contains Carbon, Nitrogen, Chlorine and Bromine. It melts at 160–61° to a colourless liquid which slowly volatilises as the temperature is raised. It sublimes above 100°. It dissolves in ether, carbon disulphide, carbon tetrachloride, petroleum ether and very readily in chloroform, benzene, and acetone. Alcohol decomposes it with the formation of cyanuric acid. It is insoluble in cold water, but dissolves in hot water. Heated with water at 100–20°, cyanuric acid, HCl and HBr are formed. The substance has a strong, pungent, and irritating odour causing tears in the eyes.

The carbon was estimated by the usual method, and the nitrogen by Dumas method. The total halide was estimated by Piria and Schiff's method, and thence the two halogens were estimated separately by Moser and Miksch method of heating the combined silver halides with pure dry ammonium bromide (to convert the chloride into bromide). On analysis the substance was found to have the composition, Cl = 47·4%, Br = 12·85%, N = 21·43% and C = 18·31%. From the percentage composition, the calculated formula comes to $C_9N_9Cl_8Br$ with a molecular weight of 597. But

the molecular weight determined by the cryoscopic method using benzene as the solvent comes to only 206.

0·2298 gm. of substance dissolved in 24·8310 gm. of benzene gave a depression of 0·225° C. (Mol. Weight = 205·6).

0·2477 gm. of substance dissolved in 23·9520 gm. of benzene gave a depression of 0·251° C. (Mol. Weight = 206).

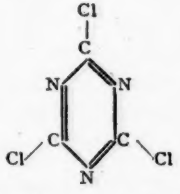
The melting point of substance, however, remains unchanged when crystallised from acetone and carbon tetrachloride and also after subliming.

It is probable the substance is a double compound of two molecules of cyanuric chloride, $C_3N_3Cl_3$, and one molecule of monobromo cyanuric chloride, $C_3N_3Cl_2Br$ (see below), which dissociates in benzene into two molecules of $C_3N_3Cl_3$ and one of $C_3N_3Cl_2Br$. This will explain the observed molecular weight (206) in benzene which is nearly one-third the theoretical (597). It is further proved that the substance is a definite compound from the melting point determinations of mixtures of the two compounds, $C_3N_3Cl_3$ and $C_3N_3Cl_2Br$. For, the melting points of mixtures of $C_3N_3Cl_3$ and $C_3N_3Cl_2Br$ mixed in proportions slightly higher and lower than the theoretical ratio 2:1 were lower than the m.p. (160°) of the substance ($C_9N_9Cl_8Br$).

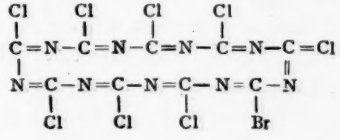
m.p. of a mixture of 0·0241 gm. (70·87%) of $C_3N_3Cl_3$ and 0·0099 gm. (29·13%) of $C_3N_3Cl_2Br$ was 156° C.

m.p. of a mixture of 0·01103 gm. (48·52%) of $C_3N_3Cl_3$ and 0·0117 gm. (51·48%) of $C_3N_3Cl_2Br$ was 150° C.

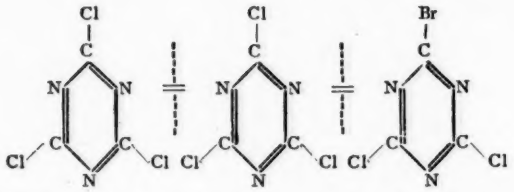
Cyanuric chloride is given a cyclic ring structure as 2 · 4 · 6 · trichloro 1 · 3 · 5 · triazin (Chattaway, 1902).



In a similar manner the constitution of $C_9N_9Cl_8Br$ can be expressed either as



or



The second formula can easily account for the observed dissociation of the compound into three simple molecules in benzene.

II. Action of Hydrobromic Acid on Cyanuric Chloride

By the action of aqueous hydriodic acid (57%, constant boiling point acid) on cyanuric chloride in the cold, Klason (1886) observed that besides cyanuric iodide, the compound monochloro cyanuric iodide, $C_3N_3I_2Cl$, was also formed as an intermediate product. This was obtained as white feathery crystals by heating the cyanuric iodide formed at about 360°. So it was expected that by a similar treatment of cyanuric chloride with hydrobromic acid (47% constant boiling point acid) the corresponding bromo compound could be obtained. But instead of the bromo compound $C_3N_3Br_2Cl$, only $C_3N_2Cl_2Br$ was obtained.

Experimental

Cyanuric chloride was prepared according to the methods of Klason (1886) and Fries (1886).

Into a flask containing pure dry chloroform, chlorine was passed until saturation. Then chlorine and hydrogen cyanide were both passed simultaneously, keeping the chlorine always in excess and applying strong cooling throughout the experiment. After 12 hours the flask was fitted with a condenser and refluxed until the excess of chlorine, HCl and the unpolymerised CNCl had all escaped. Then the chloroform was distilled off, when a residue of long needle-shaped crystals was got. The product was recrystallised from petroleum ether and dried in a desiccator.

To about a gram of the pulverised cyanuric chloride about 6–8 c.c. of 47% hydrobromic acid were added and constantly stirred. After every three hours, the acid was removed by decantation, fresh acid added and again stirred constantly. The reaction was thus continued for 24 hours. Then it was filtered, washed and dried in a desiccator. The dried product was heated up to 150° when prismatic crystals sublimed. After resubliming it was used for analysis.

This substance contains Carbon, Nitrogen, Chlorine and Bromine. Most of it sublimes below 200°, only a little melts at 210° which slowly volatilises as the temperature is raised further. It dissolves in all the usual organic solvents. Alcohol decomposes it with the formation of cyanuric acid. It is insoluble in cold water, but when heated with water at 120°, cyanuric acid, HCl and HBr are formed.

On analysis the substance is found to have the composition Cl = 30·4%, Br = 34·31%, and N = 18·22%; $C_3N_3Cl_2Br$ requires Cl = 30·98%, Br = 34·92%, and N = 18·37%.

The m.p. of substance remains unchanged when crystallised from chloroform.

The non-volatile residue left behind on heating the washed and dried product of the reaction of hydrobromic acid on cyanuric chloride, also contained carbon, nitrogen, chlorine and bromine. The quantity of substance available was too small for analysis. It did not melt nor sublime upto 280° C.

Further work is in progress.

The author is deeply indebted to late Professor Edward Barnes under whose direction and guidance the work was carried out.

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SPREADING COEFFICIENTS OF NEKAL BX SOLUTIONS

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Introduction

Wetting agents are being extensively used in several of the processes of the textile industry such as kier boiling, dyeing and finishing. The wetting agents bring about thorough wetting and thereby ensure uniformity in the treatment of fabrics. They also accelerate the penetration of liquids into the fabric and thereby increase the speed of operation. A large number of wetting agents having varying degrees of efficiency are now commercially available.

The evaluation of wetting agents is of great importance to the producer as well as the consumer. Several methods are available. Most of the methods however are of a semi-quantitative character. Though they are useful for industrial purposes, they fail to give an exact measure of the wetting property. Theoretically, the determination of the spreading coefficient of the wetting agent solution on the grey yarn should give a precise idea of the wetting power. But, the measurement of this quantity is beset with many difficulties since the system involves solids. Irreproducible kinetic effects, complications due to the roughness of the surface,[1] and friction effects at the meniscus render difficult an accurate determination of the contact angles in such systems. It is therefore preferable to find out the spreading coefficients of wetting agent solutions on a hydrophobic liquid such as a mineral oil and assess the wetting properties.

Cupples[2] has determined the spreading coefficients by measuring the surface tension of the oil γ_o, surface tension of the aqueous solution γ_w and the interfacial tension γ_{wo} of the oil-aqueous solution interface. The spreading coefficient for water on oil is given by the equation:

$$S_{wo} = \gamma_o - \gamma_w - \gamma_{wo}.$$

The interfacial tension values obtained by the ring method are rendered uncertain owing to the frequent occurrence of finite contact angles. We have therefore adopted the free lens technique of Langmuir[3] for measuring

the spreading coefficients of nekal BX solutions. The method consists in measuring the diameters of oil lenses formed from known amounts of oil. If V is the volume of oil employed and R is the radius of the lens formed, one can get the value of t_∞ by plotting the values of $\frac{V}{\pi R^2}$ against $\frac{1}{R}$ and extrapolating to $\frac{1}{R} = 0$.

Experimental

Purification of materials.—The nekal BX (sodium dialkyl naphthalene sulphonate) used was a purified specimen prepared from the commercial sample by the following method.[4] 25 g. of dry commercial quality nekal BX were dissolved in 250 c.c. of alcohol. The solution was allowed to stand overnight in a tall cylinder. The clear supernatant liquid was filtered and the filtrate was concentrated and finally evaporated to dryness. The residue was dried in a hot air oven at 100° C. for 3 to 4 hours. The material was powdered and bottled while still hot. The paraffin oil used in these investigations was Evan's " Liquid Paraffin ". It was used without further purification as it was found to have the following characteristics. It did not spread on water but formed a lens. It did not develop any surface pressure as indicated by the surface pressure balance and it did not give rise to any appreciable surface film when put on water.

Apparatus

It is to be pointed out that the systems dealt with in this paper are those which exhibit a variation of the surface properties with time.[4] In order to get comparable and reproducible results, it is necessary to work with surfaces of definite age. In order to enable this, a special shallow glass trough $2' \times 1\frac{1}{2}'$ was constructed by fixing a beading of $\frac{1}{4}''$ glass strips, on a $\frac{1}{4}''$ glass plate by means of a high grade paraffin wax. The edges of the trough were paraffined so that the surface of solutions in the trough could be swept by barriers as in surface film work. Paraffined glass strips were used as barriers. The paraffin oil lenses were photographed from above, using a double extension camera with a Ziess Tessar f/4·5 lens of focal length 13·5 cm. stopped down to f/8. Exposure of 1/5 to 1/2 second was given. The paraffin oil lens was illuminated from the bottom by means of a 100 watt electric lamp. A sheet of ground glass was interposed between the oil lens and the lamp. As the paraffin oil has a higher refractive index than water, it can easily be shown that the light from the extended source under the conditions of our experiments gets refracted in such a way that the boundary of the oil lens comes out very sharp in the photograph. Distance between the object and the camera was

about 22″ and the distance between the lens and the source of light was 24″. To find the relationship between the size of the object and the size of the image, an accurate glass scale was photographed from the same distance. An examination of the photograph of the scale showed that the errors due to spherical aberration were negligible. The sensitive material used was Ilford H.P. 2 plates and they were hardened during development.

Procedure.—The trough was completely filled with the solution. The surface was then cleared with paraffined barriers. The surface tension of the solution at 11, 13 and 15 minutes after clearing were determined by the ring method using Du Nouy tensiometer in its modified form.[4] In calculating the surface tension the corrections of Harkins and Jordan[5] have been applied. The values obtained are given in Table II and Fig. 1.

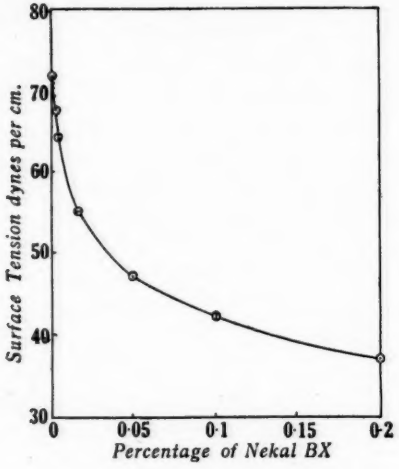

FIG. 1

Surface Tension of Nekal BX Solutions (age of Surface 11 minutes)

Before photographing, the surface was cleared once again and immediately a known weight of paraffin oil was added. Eleven minutes after clearing, the oil lens was photographed. The diameter of the lens on the negative was measured correct to 0·001 cm. using a travelling microscope and taking the mean of 2 to 4 even diameters. The work was done in a room free from droughts and at a temperature of 27·5° ± 1·0° C.

The surface tension of the paraffin oil was determined by the maximum bubble pressure technique as developed in this laboratory.[4]

The values of $\frac{V}{\pi R^2}$, $\frac{1}{R}$, and t_∞ (extrapolated) obtained in the several systems examined, are given in Table I.

The values of the spreading coefficient of oil on water can be calculated by the equation

$$S_{ow} = -\frac{g\,\rho_2\,(\rho_1 - \rho_2)\,t_\infty{}^2}{2\,\rho_1}$$

where g is the acceleration due to gravity, ρ_1 the density of water and ρ_2 the density of the paraffin oil used (0·885).

From these values the spreading coefficient of water on oil is calculated by the equation

$$S_{wo} = S_{ow} - 2\,\{\gamma_w - \gamma_o\}$$

where γ_w and γ_o are the surface tensions of the aqueous solution and paraffin oil respectively.

The interfacial tension γ_{wo} of the aqueous solution-oil interface has been calculated by the equation

$$\gamma_{wo} = -S_{ow} + \gamma_w - \gamma_o.$$

The adhesion tension of water against oil is given by the equation

$$A_{wo} = \gamma_o - \gamma_{wo}.$$

The values of all these quantities for nekal BX solutions of different concentrations are given in Table II and Figs. 2 to 5.

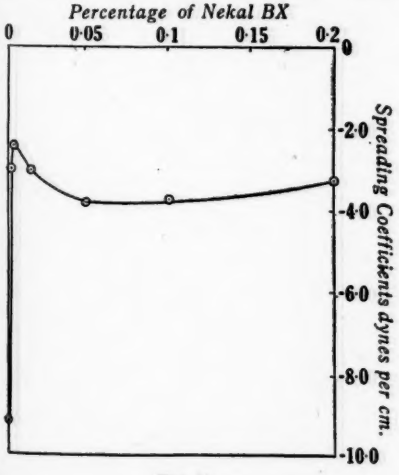

FIG. 2.
Spreading Coefficients of Paraffin Oil on Nekal BX Solutions.

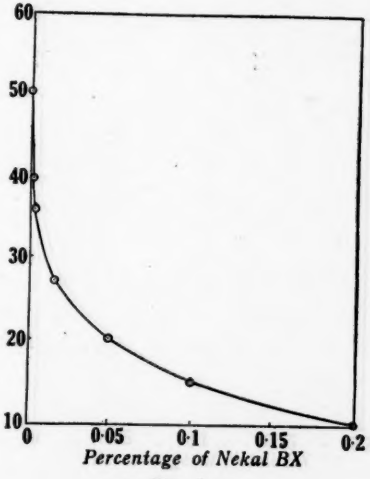

FIG. 3
Interfacial Tension of Paraffin Oil Nekal BX Solution Interface

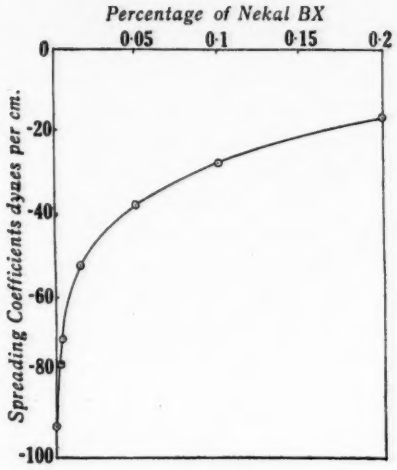

FIG. 4

Spreading Coefficients of Nekal BX Solutions on Paraffin Oil.

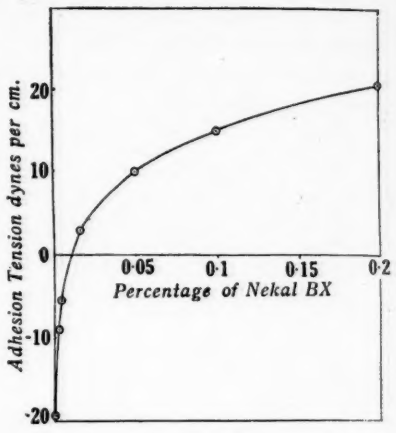

FIG. 5

Adhesion Teusion of Nekal BX Solutions (Age in Interfaces 11 minues.)

TABLE I

Concentration of Nekal BX 0·00%		Concentration of Nekal BX 0·0025%		Concentration of Nekal BX 0·005%		Concentration of Nekal BX 0·017%	
1/R	$\frac{V}{\pi R^2}$	1/R	$\frac{V}{\pi R^2}$	1/R	$\frac{V}{\pi R^2}$	1/R	$\frac{V}{\pi R^2}$
0·171	0·427	0·161	0·151	0·190	0·185	0·175	0·214
0·160	0·427	0·156	0·156	0·153	0·194	0·147	0·226
0·156	0·428	0·118	0·179	0·122	0·153	0·132	0·223
0·102	0·430	0·116	0·190	0·111	0·202	0·099	0·235
0·000	0·434*	0·000	0·250*	0·093	0·219	0·091	0·237
				0·000	0·226*	0·000	0·262*

* Extrapolated.

TABLE I (*Contd.*)

Concentration of Nekal BX 0·05%		Concentration of Nekal BX 0·1%		Concentration of Nekal BX 0·2%	
1/R	$\frac{V}{\pi R^3}$	1/R	$\frac{V}{\pi R^3}$	1/R	$\frac{V}{\pi R^3}$
0·177	0·227	0·183	0·239	0·183	0·256
0·160	0·236	0·151	0·246	0·139	0·257
0·139	0·245	0·136	0·243	0·111	0·258
0·112	0·244	0·105	0·256	0·000	0·262*
0·092	0·254	0·094	0·261		
0·000	0·282*	0·000	0·278*		

* Extrapolated.

TABLE II

Concentration of Nekal BX weight %	γ_w dynes/cm.	S_{ow} dynes/cm.	γ_{wo} dynes/cm.	S_{wo} dynes/cm.	A_{wo} dynes/cm.
0·0000	72·0	− 9·10	50·3	− 91·5	− 19·5
0·0025	67·6	− 3·00	39·8	− 76·6	− 9·0
0·005	64·6	− 2·46	36·3	− 70·1	− 5·5
0·017	55·5	− 3·31	28·0	− 52·7	+ 2·8
0·05	47·9	− 3·84	20·9	− 38·0	+ 9·9
0·1	42·9	− 3·73	15·8	− 27·9	+ 15·0
0·2	37·7	− 3·30	10·2	− 17·1	+ 20·6

Discussion

1. *Spreading coefficients of oil on aqueous solutions.*—A glance at Fig. 2 shows that the presence of nekal BX to the extent of 0·005% increases tremendously the spreading of paraffin oil. Further increase in concentration does not considerably affect the spreading though the minimum in the curve is followed by a small flat maximum. The first sudden increase in the spreading is presumably due to the solute molecules accumulating more easily at the oil-aqueous solution interface than at the air-aqueous solution interface. At higher concentrations, the solute accumulates to nearly the same extent

at both the interfaces. It may therefore be concluded that small quantities of nekal BX very much improve the spreading properties of oils on polar surfaces. This fact appears to be of great interest in lubrication problems.

2. *Spreading coefficients of aqueous solutions on oil and the adhesion tensions.*—The spreading coefficients of aqueous solutions become less and less negative as the concentration of nekal BX is increased (Fig. 4). The wetting power of the solutions is therefore increased by raising the concentration of nekal BX. It is however to be noted that the spreading coefficient does not become positive even at the highest concentrations tried. It appears therefore that the process of wetting of the grey yarn by these solutions (assuming that the wetting characteristics of grey yarn and liquid paraffin are similar) is not by spreading but takes place by creeping of the liquid into the capillary spaces. This tendency is determined by the adhesion tension of the aqueous solution against oil which is given by $\gamma_o - \gamma_{wo}$ and not by the spreading coefficients. The values of adhesion tension is negative for water and for dilute solutions and becomes positive only with concentrations higher than 0·0%15 of nekal BX (*vide* Fig. 5).

The adhesion tension of aqueous solution against oil

$$A_{wo} = \gamma_o - \gamma_{wo} = 2\gamma_o - \gamma_w + S_{ow}$$

Since S_{ow} is more or less constant at all concentrations of nekal BX (except with the most dilute solutions) it is clear that the adhesion tension is mainly determined by the value of γ_w. Thus the surface tension lowering may be taken as a rough measure of the wetting power. This conclusion can also be justified on theoretical grounds. A solute which strongly lowers the surface tension of water is strongly adsorbed at the surface. The high adsorption is caused by the presence of hydrophobic portions in the solute molecule. Such a solute can also be expected to be adsorbed at the mineral oil-water interfaces. So the interfacial tension would be low. The adhesion tension $\gamma_o - \gamma_{wo}$ would be correspondingly high. Thus the surface tension lowering would run parallel to the values of the adhesion tension and would therefore be a rough measure of the wetting power.

Summary

The spreading coefficients of paraffin oil on nekal BX solutions have been determined by the floating lens technique of Langmuir. These measurements combined with the surface tension of the aqueous solutions give an exact idea of the wetting characteristics of the solutions. A rough measure of the wetting power is shown to be given by a measurement of the surface tension of the aqueous solution.

It is shown that small quantities of nekal BX greatly improve the spreading qualities of oils on polar surfaces.

The spreading coefficients of nekal BX solutions are found to be negative even at the highest concentrations tried. It is therefore suggested that the wetting takes place by penetration and not by spreading. Thus, the adhesion tension of the aqueous solutions against oil gives a more correct measure of the wetting power.

In conclusion, the authors wish to thank Professor B. Sanjiva Rao, for his kind and helpful interest in the work.

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A STUDY OF THE RAMAN EFFECT IN SEVENTEEN OPTICAL GLASSES

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1. Introduction

Raman effect investigations on glass are not very numerous, and further work on the subject is greatly to be desired as our knowledge of the structure of glass is far from being complete at the present time. Amongst the more important investigations in this field are those of Raman (1928), Gross and Romanova (1929), Bhagavantam (1931), Kujumzelis (1935), and Langenberg (1937). Prof. Raman noticed that the spectrum of glass generally consists of diffuse bands and not sharp lines. Gross and Romanova studied two Russian optical glasses, one a crown and the other a flint, as well as amorphous and crystalline quartz and recorded a series of bands in these glasses and in fused quartz, and conlcuded that these bands correspond roughly to the lines observed in the case of crystalline quartz. They also noted that the bands are more intense with flint than with crown glass.

Bhagavantam studied a series of ten optical glasses from the firm of Schott of Jena. He recorded the presence of a band at $460 \rightarrow 520$ cm.$^{-1}$ with all the glasses and of another band at $780 \rightarrow 800$ which occurs with nearly all of them. He also noticed that the feeble band at 1080 observed with the crown glasses is less intense than the $460 \rightarrow 520$ band, and that the two much stronger bands at 1000 and 1080 exhibited by the flint glasses are more intense than the band at $460 \rightarrow 520$, though the latter also gained in intensity in passing from the crown to the flint glasses. Bhagavantam further noticed a band at 640 in a light baryta flint glass, and a band at 650 in a dense boro-silicate crown ; the latter also exhibits a band at 340. With some of the glasses a feeble band at 1320 was also observed.

Kujumzelis carried out a systematic study with nineteen optical glasses also from the firm of Schott, as well as with fused quartz and fused boron trioxide. He drew attention to an important feature, namely, that the Raman spectrum of glass includes a continuum stretching from the exciting line towards longer wave-lengths and showing a fairly well-defined limit at about

530 wave numbers from the exciting line. This is traversed, however, by subsidiary bands, especially in the vicinity of its outer edge. All the lead glasses studied by Kujumzelis showed, in addition, a weak band in the 600 region, a somewhat stronger band at about 780, and four bands within the frequency range 900 to 1200, of which the two central ones were the most intense, the positions of these latter shift towards the exciting line with increasing lead content of the glass. Fused silica showed bands at 230 → 450 and a continuum having a limit at 500, bands at 607, 780 → 840, 1030 → 1090 and 1160 → 1230. Pure boric oxide glass showed a sharp line at 808. The work of Kujumzelis showed that the spectrum of glass is strongly influenced by its chemical composition, both as regards the position and the intensity of the bands, and especially by the proportion of boric and lead oxides to silica. Langenberg studied twenty-six optical glasses including pure boric oxide glass and fused quartz, all except the last being from the firm of Schott. While confirming the results of Kujumzelis, he attempts to attribute the frequencies of the various observed bands with the vibration frequencies of the several chemical components in the glass ; as for instance to the SiO_4-ion in the silicate glasses and to the BO_3-ion in the borate glasses.

Reference may be made also to the recent work of Matossi and Bluschke (1938), who have studied the infra-red reflection spectra of about 23 glasses of different compositions. All the silicate glasses show broad bands of which the two stronger have their maxima at about 9 μ and between 22 to 23 μ respectively. Weaker bands are also observed at 8·8 μ, 12·8 μ, and 20·9 μ for fused quartz glass ; at 7 μ and 14·8 μ for silica-barium glasses with boron content ; and at 7 μ, 11·5 μ and 14·8 μ for borate glasses containing lead.

The present paper records the results of a study of the Raman spectra of seventeen optical glasses, manufactured by the firm of Schott at Jena.

2. *Specimens Studied*

Table I gives the list of the glasses studied, as also their composition and density furnished by the manufacturers. They were all in the form of rectangular slabs (3 × 3 × 2 c.c.) with all except two of their end faces polished. These were the same specimens with which R. S. Krishnan (1936) carried out in this Laboratory his investigation on " Scattering of Light in Optical Glasses". The refractive indices of the specimens given in Table I are the values as measured by him with a Pulfrich refractometer. The Raman spectrum of crystalline quartz in the form of a cylinder of length 5 cm. and diameter 2·5 cm. has also been recorded for purpose of comparison.

TABLE I

Serial Number	Melting Number	Glass contains traces of Al_2O_3, Fe_2O_3, As_2O_3 and Oxides in		Density	Refractive index μ_D
		more than 10%	less than 10%		
1	25188	SiO_2, B_2O_3, Al_2O_3, K_2O	Na_2O, F	2·3	1·4670
2	18415	SiO_2, B_2O_3, K_2O	Al_2O_3	2·3	1·4925
3	16776	SiO_2, K_2O	Al_2O_3, Na_2O, CaO	2·4	1·5022
4	23975	SiO_2, B_2O_3, ZnO	Al_2O_3, Na_2O	2·5	1·5095
5	24906	SiO_2, B_2O_3	Na_2O, K_2O, BaO	2·5	1·5269
6	22601	SiO_2, B_2O_3, Sb_2O_3	Al_2O_3, Na_2O, K_2O	2·7	1·5294
7	23125	SiO_2, Na_2O, PbO	ZnO	2·7	1·5370
8	22638	SiO_2, PbO	Na_2O, K_2O	2·9	1·5449
9	24464	SiO_2, ZnO, BaO	B_2O_3, Na_2O, K_2O, PbO	3·1	1·5697
10	19510	SiO_2, PbO	Na_2O, K_2O	3·2	1·5698
11	23355	SiO_2, B_2O_3, BaO	Al_2O_3, Na_2O	3·3	1·5892
12	20672	SiO_2, PbO	B_2O_3, Na_2O, K_2O	3·4	1·5983
13	22986	SiO_2, BaO, PbO	Na_2O, K_2O, ZnO	3·5	1·6163
14	23441	SiO_2, PbO	Na_2O, K_2O	3·9	1·6473
15	23497	SiO_2, BaO, PbO	Na_2O, K_2O, ZnO	3·9	1·6498
16	23850	SiO_2, PbO	Na_2O, K_2O	4·4	1·7130
17	23590	SiO_2, PbO	Na_2O, K_2O	5·1	1·7850

3. *Experimental Arrangements*

All the specimens were investigated with a Fuess glass spectrograph of of large light-gathering power. Each of the glass slabs was illuminated by placing the mercury arc near its side and the scattered light was focussed directly on to the slit of the spectrograph. Most of the specimens showed strong fluorescence which masked the Raman spectrum. This disturbance was effectively eliminated by cutting out the 4046 Å region of the mercury arc with a suitable filter ; a saturated solution of $NaNO_2$ (sodium nitrite) in water kept in a specially made pyrex glass cell was found to serve the purpose very well. As the glass No. 17 was coloured yellow, no filter was necessary in this case ; 4358 Å being the exciting wave-length. Ilford selochrome plates were used. The photographic plates were measured on a micrometer by comparison with the iron arc spectrum taken along with the spectra

on the plates. In the case of the weak and diffuse bands, the measurements were necessarily rough.

The continuum following the exciting line, which will be mentioned in the next section, is shown to be a genuine Raman effect, and not a case of fluorescence by taking the glasses which are not strongly fluorescent and utilising only the 4046 Å line of the mercury arc as the exciting line and cutting out the 4358 Å radiation with a concentrated solution of Iodine in CCl_4 before entry of the light into the glass. The continuua are then found to accompany the 4046 Å line, exhibiting the same limit for the frequency shift, while the continuua following the 4358 Å line disappear.

4. Results

The Raman spectra obtained in the case of the glasses consist in general of broad and diffuse bands, as will be seen in Plate VII. It is considered advantageous to give the frequency displacements and the intensities of the bands in the form of graphical representations, in Figs. 1 and 2 ; the intensities of the various bands in each case are drawn relative to the most

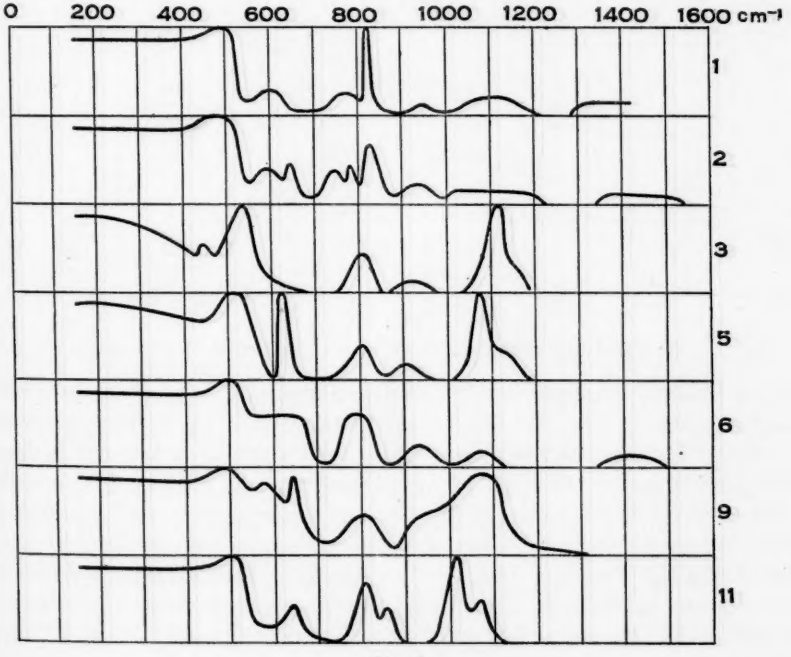

FIG. 1

Graphical Representation of the Raman Effect of Silica Glasses

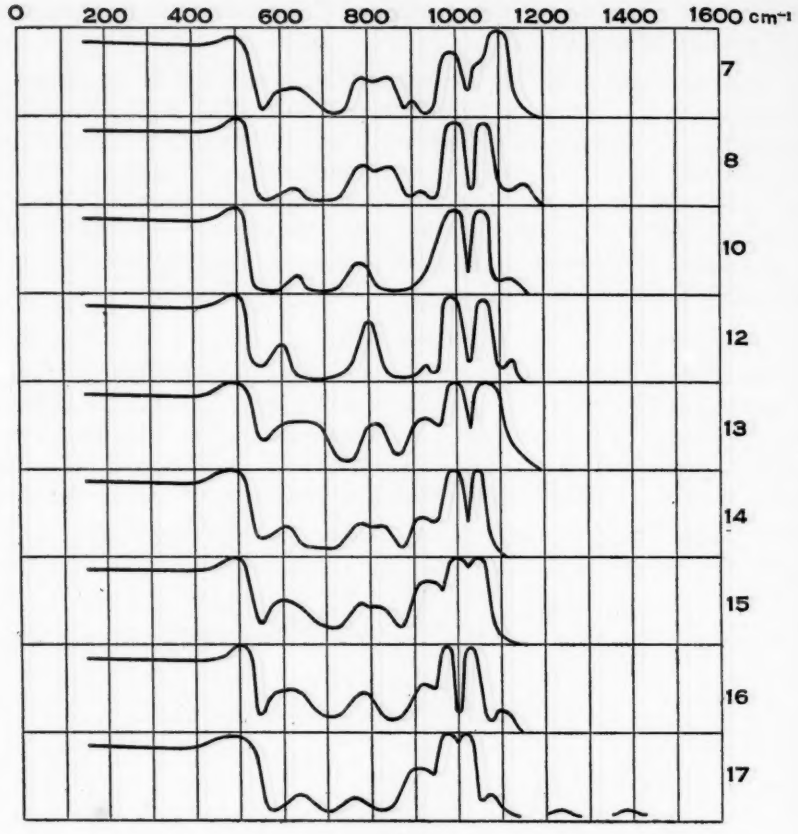

FIG. 2
Graphical Representation of the Raman Effect of Si-Pb Glasses

intense band of that specimen. The actual measurements of the bands are given in Tables II and III. The general characteristics of the Raman spectra are similar for glasses of the same qualitative composition, but vary in detail from glass to glass. As reported by Kujumzelis, each glass exhibits a continuum closely following the exciting line and ending abruptly with a limit at about 530 wave numbers. These continuua end with a sharp limit in glasses containing PbO, while they do not end so sharply and are followed by a certain haziness beyond this limit in the other glasses, especially those which do not contain PbO. This can be seen to be so in the case of glasses of Nos. 3, 5, 6, 9 and 11 of the present study. That these continuua are due to genuine Raman effect and not due to fluorescence has been demonstrated, as already

TABLE II

Frequency Shifts and Approximate Intensities of the Raman Bands in Silica Glasses

1	2	3	5	6	9	11
– 512 Lt.	– 517 Lt.	– 555 Lt.	– 558 Lt.	– 520 Lt.	– 555 Lt.	– 528 Lt.
434– 512 (v.s.)	447– 517 (v.s.)	450 (f.s.)				495– 528 (s.)
512– 633 (e.w.)	517– 644 (e.w.)	523– 555 (v.s.)	495– 558 (s.)	520– 670 (f.s.)	580 (s.)	
603 (w.)		555– 675 (w.)	634 (v.s.)		640 (sh.)	639 (w.)
722– 816 (e.w.)	768 (w.)	771– 830 (f.s.)	726 (w.)	780– 820 (f.s.)	768– 844 (f.s.)	673 (w.)
816 (sh.)	803– 840 (f.s.)					810 (s.) 845 (f.s.)
931 (w.)	890– 969 (w.)	852– 995 (w.)	904 (w.)	930 (w.)	908–1143 (w.)	976–1042 (s.)
1014–1186 (w.)	1012–1240 (e.w.)	1073–1136 (v.s.)	1037–1086 (f.s.)	1070 (w.)	1036–1116 (v.s.)	1065 (f.s.)
		1050–1194 (s.)	1086–1198 (w.)		1150–1300 (e.w.)	1133 (w.)
	1350–1670 (e. w.)			1340–1500 (e.w.)		1258–1460 (e.w.)

TABLE III

Frequency Shifts and Approximate Intensities of the Raman Bands in Si–Pb Glasses

7	8	10	12	13	14	15	16	17
– 529 Lt.	– 528 Lt.	– 528 Lt.	– 526 Lt.	– 530 Lt.	– 528 Lt.	– 531 Lt.	– 528 Lt.	– 530 Lt.
588– 668 (w.)	640 (w.)	632 (w.)	603 (w.)	593– 702 (f.s.)	619 (w.)	610 (w.)	573– 673 (w.)	639 (e.w.)
759– 868 (f.s.)	760– 870 (f.s.)	781 (f.s.)	810 (f.s.)	772– 843 (f.s.)	769– 847 (f.s.)	754– 802 (f.s.)	747– 811 (f.s.)	778 (w.)
895 (w.)	908 (w.)		928 (e.w.)	897– 961 (s.)	894– 946 (f.s)	894– 961 (s.)	894– 947 (f.s.)	879– 946 (s.)
967–1024 (s.)	978–1017 (v.s.)	968–1024 (v.s.)	964–1017 (v.s.)	966–1024 (v.s.)	964–1015 (v.s)	969–1019 (v.s.)	947– 990 (v.s.)	949– 990 (v.s.)
1043 (w.)					1019–1062 (v.s)	1024–1086 (v.s.)	1014–1068 (vs.)	993–1037 (v.s.)
1063–1123 (v.s.)	1041–1085 (v.s.)	1037–1085 (v.s.)	1037–1085 (v.s.)	1045–1120 (v.s.)				
	1177 (w.)	1130 (w.)	1131 (w.)	1120–1200 (e.w)			1100 (e.w.)	1086 (w.)
								1256 (e.w.)
								1383 (e.w.)

Lt., Limit; e.w., extremely weak; w., weak; f.s., fairly strong; v.s., very strong; s., strong; sh., sharp.

mentioned, by the use of filters. In the sufficiently well exposed plates the continuua also appear on the shorter wavelength side of the exciting line, the limiting frequency shift being the same as for the one on the longer wavelength side. In the glass No. 1, which contains both boric oxide and fluorine the band at 800 is sharp and intense, and the continuum stretching upto about 500 is strong, while the other bands are relatively weak and diffuse. The same features are also observed in glass 2, which is of similar composition but for the omission of fluorine, except that the 800 band is not now so marked. A comparison between the glasses 3 and 5 is specially interesting, the latter containing boric oxide and the former not. In the silica-alkali glass, the continuum is weak, but a band at 540 is strong and well defined, while in the glass containing boric oxide, the continuum is stronger but the band at 520 is not so well defined. On the other hand, in glass 5, the band at 634 is strong, while in glass 3, it is not noticeable. In both glasses the band in the 1000–1200 region is strong, but more so in glass 3. Glass 4 was too strongly fluorescent to give any useful results. Glass 11 which is a heavy one containing barium but no lead shows a definite shift of the band at 1000 towards the exciting line which is very significant in view of the analogous results shown by the lead glasses, which we shall comment upon. The Si-Pb glasses exhibit a characteristic Raman spectrum, having an intense continuum with a sharp limit, this limit remaining the same for all the glasses of the series irrespective of lead content, as also two weak and diffuse bands at 600 and 800 and two very prominent bands in the 950→1100 region, with weaker bands on either side of them. Glass 7 appears also to exhibit a weak band at about 1050 between the two stronger bands. It is noteworthy, as has already been observed by Kujumzelis, that with increasing lead content the two intense bands in the 950→1100 region are gradually displaced towards the exciting radiation, while at the same time they approach nearer each other. The presence of BaO in the glasses has the effect of making these two strong bands more intense, as also to cause them to approach each other and shift towards the exciting line but to a lesser extent than for lead glasses; it appears also to result in an enhancement of the intensity of the bands at 600, 800 and of the weak one at 930.

The interpretation of these results will be discussed in a later communication.

In conclusion, the author takes this opportunity to thank Prof. Sir C. V. Raman for his keen interest in this work.

Summary

The Raman spectra of a representative collection of seventeen optical glasses of varying composition and density were investigated. The observed

results are given in the tables as well as in the form of graphical representations and the spectra are also reproduced in the Plate, and their relation to chemical composition is pointed out. A resumé of the results of the previous investigators in this field is also given. The continuua that follow the exciting line in the spectra are shown to be due to a genuine Raman effect and not a case of fluorescence. The work broadly confirms the experimental results of Kujumzelis. Important features, as for instance the influence of barium and lead oxides on the spectra are also emphasised. The effect of the presence of boric and lead oxides on the distribution of intensity on the continuum is a noteworthy feature brought out by the present investigation.

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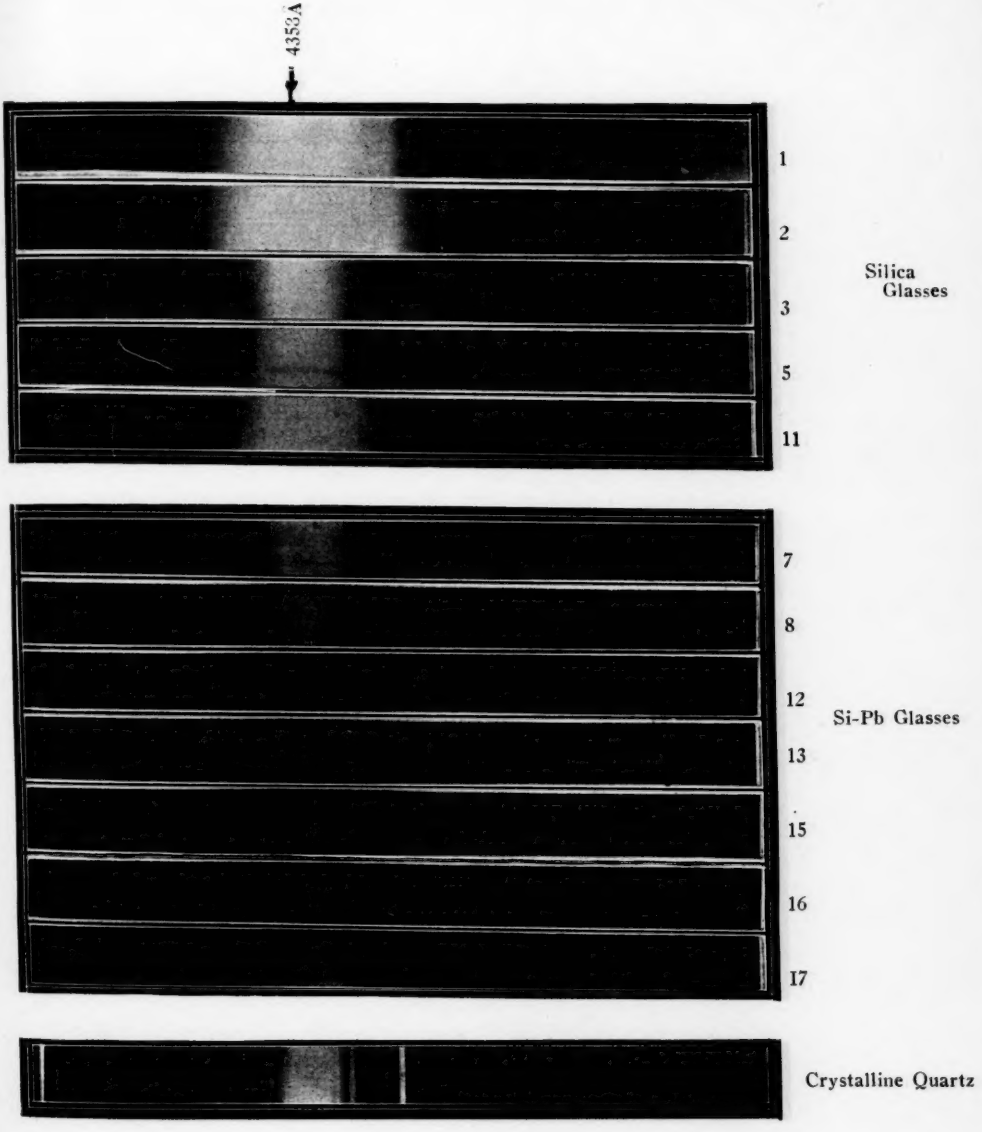
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1
2
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11
Silica Glasses
7
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12
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17
Si-Pb Glasses
Crystalline Quartz

THE GRAVITATIONAL EQUATIONS OF MOTION IN RELATIVITY

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§1. In a recent paper, which will here be referred to as E. I. H., Einstein, Infeld and Hoffmann[1] have given a new relativity theory of gravitation. It marks an important departure from the well-known general theory which the authors describe as classical relativity. The essence of the new theory lies in its possession of the three ideal features which were the desiderata of the earlier theory. Einstein[2,3,4] has stated them in a number of publications during the last six years or so. They may be expressed briefly as follows : (A) Field equations should give both matter and motion, (B) the geodesic postulate[5] being redundant should have no place in the field theory, (C) the duality of the field energy and matter[4,6] being unsatisfactory the problem of gravitating matter should be solved without the use of an extraneous energy-momentum tensor such as $T_{\mu\nu}$. The three ideas are interconnected. It is essential to understand them if the significance of the results arrived at in this paper is to be grasped.

A logical working out of these ideas which covers the entire domain of phenomena of general relativity is a definite advance over the latter theory inasmuch as a greater economy and generality are achieved in the choice of the number and nature of the basic postulates and hypotheses. The solution of the problem of n bodies given in E. I. H. is such a logical working out of the new ideas. Thus the gravitational equations of motion are obtained purely from the field equations,

$$G_{\mu\nu} = 0, \tag{1}$$

the solution being subject to the condition that the space-time frame is flat at infinity. This method must be distinguished from the earlier and unsatisfactory attempts of de Sitter, Levi Civita and Eddington and Clark[7] who had to use not only the more complicated equations,

$$G_{\mu\nu} - \tfrac{1}{2} G g_{\mu\nu} = - kT_{\mu\nu}, \tag{2}$$

but the equations of geodesics also, *viz.*,

$$\frac{d^2x^\mu}{ds^2} + \Gamma^\mu_{\alpha\beta} \frac{dx^\alpha}{ds} \frac{dx^\beta}{ds} = 0. \tag{3}$$

(The equations so far written appear in the usual notation and therefore no attempt will be made to define the various symbols.) The latter procedure is in contravention of Einstein's ideas and it introduces the difficulties of infinite self-energy which are quite common in the quantum theories of fundamental particles.

§2. The problem[5] that we take up is this. Following the procedure of E. I. H. one gets as a solution of (1),

$$g_{\mu\nu} = g_{\mu\nu}(m_1, m_2, \ldots m_n) \tag{4}$$

and the $3n$ equations of motion of the particles are obtained, those of m_1 being, say,

$$f^m(m_1, m_2, \ldots m_n) = 0 \qquad m = 1, 2, 3. \tag{5}$$

For the line-element given by (4) we have the equations of geodesics which with the time co-ordinate τ as the independent variable can be cast into the form

$$g^m(m_1, m_2, \ldots m_n) = 0 \qquad m = 1, 2, 3. \tag{6}$$

If we put $m_1 = 0$ in (5)

$$f^m(0, m_2, \ldots m_n) = 0 \tag{7}$$

are the equations of a particle of zero mass in the field of $n-1$ particles. If, however, the geodesic postulate were valid the required equations would be

$$g^m(0, m_2, \ldots m_n) = 0. \tag{8}$$

In general the two sets of equations, (7) and (8), would not be identical since the geodesic postulate has been weeded out as extraneous and unnecessary in the treatment of E.I.H. It is interesting to find out therefore at what stage the new equations of motion deviate from the geodesic postulate. When the necessary calculations are carried out we discover the surprising result that the equations (7) and (8) are identical in form and content to the second order of masses, that is, as far as the right-hand side of (5) is computed in E.I.H., in the two-body problem. Thus the geodesic postulate is found to be consistent with the equations of motion of the new theory at least over the first two phases of approximation. What will happen at higher approximations cannot be foretold without doing very lengthy calculations. In what follows the consistency will be established and an explanation will also be provided how it arises.

§3. Consider* the flat Galilean space given by the matrices $\eta_{\mu\nu}$ and $\eta_{\mu\nu}$ whose principal diagonals alone have non-zero members, being $1, -1,$

* A full exposition of E.I.H. will be found in the author's paper referred to as (6).

$-1, -1$ in order. x° is the time co-ordinate and x^1, x^2, x^3 are the space co-ordinates. Throughout the rest of the paper the Greek indices such as μ and ν refer to both space and time and run over 0, 1, 2, 3 while the Latin indices such as m and n take on only the spatial values 1, 2, 3. The dummy-suffix convention is resorted to wherever possible to indicate summation. Thus for the Galilean space

$$ds^2 = \eta_{\mu\nu}\, dx^\mu\, dx^\nu = (dx^\circ)^2 - (dx^1)^2 - (dx^2)^2 - (dx^3)^2. \tag{9}$$

Since the velocity of light is taken as unity in this it is convenient to use an auxiliary time co-ordinate τ so that

$$\frac{\partial\phi}{\partial x^\circ} = \lambda \frac{\partial\phi}{\partial\tau}, \tag{10}$$

where ϕ is a differentiable function of x^μ and λ is a small parameter. This makes $\partial\phi/\partial\tau$ of the same order as $\partial\phi/\partial x^m$.

The line-element of Einstein's[1] solution of the problem of two bodies of masses m_1 and m_2 runs as follows :

$$ds^2 = g_{\mu\nu}\, dx^\mu\, dx^\nu = (\eta_{\mu\nu} + h_{\mu\nu})\, dx^\mu\, dx^\nu \tag{11}$$

where,

$$h_{oo} = \lambda^2\left[-\frac{2m_1}{r_1} - \frac{2m_2}{r_2}\right] + \lambda^4\left[-m_1\frac{\partial^2 r_1}{\partial\tau^2} - m_2\frac{\partial^2 r_2}{\partial\tau^2} + 2\left(\frac{m_1}{r_1} + \frac{m_2}{r_2}\right)^2\right.$$

$$\left. + \left(\tfrac{3}{2}\dot{\eta}^s\dot{\eta}^s - \frac{m^2}{r_{12}}\right)\left(-\frac{2m_1}{r_1}\right) + \left(\tfrac{3}{2}\dot{\xi}^s\dot{\xi}^s - \frac{m_1}{r_{12}}\right)\left(-\frac{2m_2}{r_2}\right)\right] + 0\,(\lambda^6), \tag{12}$$

$$h_{on} = \lambda^3\left(\frac{4m_1}{r_1}\dot{\eta}^n + \frac{4m_2}{r_2}\dot{\xi}^n\right) + 0\,(\lambda^5), \tag{13}$$

$$h_{mn} = -\lambda^2\,\delta_{mn}\left(\frac{2m_1}{r_1} + \frac{2m_2}{r_2}\right) + 0\,(\lambda^4). \tag{14}$$

In the above expressions δ_{mn} stands for the Kronecker delta so that

$$\left.\begin{aligned} \delta_{mn} &= 0,\ m \neq n \\ &= 1,\ m = n. \end{aligned}\right\} \tag{15}$$

Also

$$\left.\begin{aligned} {r_{12}}^2 &= (\eta^m - \xi^m)(\eta^m - \xi^m), \\ {r_1}^2 &= (x^m - \eta^m)(x^m - \eta^m), \\ {r^2}_2 &= (x^m - \xi^m)(x^m - \xi^m), \end{aligned}\right\} \tag{16}$$

η^m, ξ^m being the spatial co-ordinates of m_1 and m_2 respectively at time τ. An overhead dot denotes a differentiation with regard to τ. The metric (11)

satisfies the field equations (1) only if the six equations of motion for m_1 and m_2 are satisfied. Those for m_1 run as follows :†

$$\ddot{\eta}^m - m_2 \frac{\partial (1/r_{12})}{\partial \eta^m} = m_2\lambda^2 \left\{ [\dot{\eta}^s\dot{\eta}^s + \tfrac{3}{2}\dot{\xi}^s\dot{\xi}^s - 4\,\dot{\eta}^s\dot{\xi}^s - \frac{4m_2}{r_{12}} - \frac{5m_1}{r_{12}}] \frac{\partial}{\partial \eta^m}(1/r_{12}) \right.$$
$$+ [4\,\dot{\eta}^s(\dot{\xi}^m - \dot{\eta}^m) + 3\,\dot{\eta}^m\dot{\xi}^s - 4\,\dot{\xi}^m\dot{\xi}^s] \frac{\partial}{\partial \eta^s}(1/r_{12})$$
$$\left. + \tfrac{1}{2} \frac{\partial^3 r_{12}}{\partial \eta^m \partial \eta^s \partial \eta^t} \dot{\xi}^s\dot{\xi}^t \right\} \qquad m = 1, 2, 3. \tag{17}$$

The equations of m_2 can be similarly written down by interchanging the mass-constants as also the co-ordinates. The constant λ^2 on the right-hand side may be absorbed either in m_1 and m_2 which are just constants of integration or by reverting to x° as the independent variable in place of τ.

The equations of a geodesic are given by

$$\frac{d^2x^\mu}{ds^2} + \Gamma^\mu_{\alpha\beta} \frac{dx^\alpha}{ds} \frac{dx^\beta}{ds} = 0. \tag{18}$$

Taking τ as the independent variable we restate (18) as

$$\lambda^2\ddot{x}^m + \lambda^2\dot{x}^m (d^2\tau/ds^2)/(d\tau/ds)^2 + \Gamma^m_{00} + 2\lambda\dot{x}^n \Gamma^m_{n0} + \lambda^2 \dot{x}^p\dot{x}^q \Gamma^m_{pq} = 0. \tag{19}$$

The three equations (19) together with the equation supplied by the metric, *viz.*,

$$\lambda^2 (ds/d\tau)^2 = g_{oo} + 2\, g_{no}\, \lambda\dot{x}^n + \lambda^2 g_{pq}\, \dot{x}^p\dot{x}^q \tag{20}$$

are equivalent to the four equations (18). From (19) and (20) one concludes that

$$0 = \lambda^2 \ddot{x}^m + \Gamma^m_{oo} + 2\lambda\dot{x}^n\, \Gamma^m_{no} + \lambda^2\dot{x}^p\dot{x}^q\, \Gamma^m_{pq}$$
$$- \lambda^2\dot{x}^m \cdot \tfrac{1}{2} \frac{d}{d\tau} \log (g_{oo} + 2\, g_{no}\, \lambda\dot{x}^n + \lambda^2 g_{pq}\dot{x}^p\dot{x}^q). \tag{21}$$

For the evaluation of the various terms in the last equation it is enough to note that

$$g^{\mu\nu} = \eta^{\mu\nu} + h^{\mu\nu} \tag{22}$$

where

$$h^{oo} = \lambda^2 \left(\frac{2m_1}{r_1} + \frac{2m_2}{r_2} \right) + 0\,(\lambda^4), \tag{23}$$

$$h^{on} = \lambda^3 \left(\frac{4m_1}{r_1}\,\dot{\eta}^n + \frac{4m_2}{r_2}\,\dot{\xi}^n \right) + 0\,(\lambda^5), \tag{24}$$

$$h^{mn} = \delta_{mn}\, \lambda^2 \left(\frac{2m_1}{r_1} + \frac{2m_2}{r_2} \right) + 0\,(\lambda^4). \tag{25}$$

† The notation is the same as that in Reference (6), the overhead indices being dropped for suffixes. (17) is the same as (11·67) of Reference (6).

Thus

$$\Gamma^m_{oo} = \tfrac{1}{2} g^{m\mu}\left[\frac{\partial h_{\mu 0}}{\partial x^0}+\frac{\partial h_{\mu 0}}{\partial x^0}-\frac{\partial h_{00}}{\partial x^\mu}\right]$$

$$= \lambda^2 \frac{\partial}{\partial x^m}\left[-\frac{m_1}{r_1}-\frac{m_2}{r_2}\right]$$

$$+ \lambda^4\left\{-\frac{\partial}{\partial \tau}\left[\frac{4m_1}{r_1}\dot{\eta}^m+\frac{4m_2}{r_2}\dot{\xi}^m\right]+2\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)\frac{\partial}{\partial x^m}\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)\right.$$

$$+\tfrac{1}{2}\frac{\partial}{\partial x^m}\left[-m_1\frac{\partial^2 r_1}{\partial \tau^2}-m_2\frac{\partial^2 \gamma_2}{\partial \tau^2}+2\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)^2\right.$$

$$\left.\left.-\frac{2m_1}{r_1}\left(\tfrac{3}{2}\dot{\eta}^s\dot{\eta}^s-\frac{m_2}{r_{12}}\right)-\frac{2m_2}{r_2}\left(\tfrac{3}{2}\dot{\xi}^s\dot{\xi}^s-\frac{m_1}{r_{12}}\right)\right]\right\}$$

$$+0(\lambda^6); \tag{26}$$

$$2\lambda\dot{x}^n\,\Gamma^m_{no} = 2\lambda\dot{x}^n\cdot\tfrac{1}{2}g^{m\mu}\left(\frac{\partial h_{n\mu}}{\partial x^0}+\frac{\partial h_{\mu 0}}{\partial x^n}-\frac{\partial h_{n0}}{\partial x^\mu}\right)$$

$$= -\lambda^2\dot{x}^n\frac{\partial}{\partial \tau}h_{mn}-\lambda\dot{x}^n\frac{\partial h_{m0}}{\partial x^n}+\lambda\dot{x}^n\frac{\partial h_{n0}}{\partial x^m}$$

$$= 2\lambda^4\dot{x}^m\frac{\partial}{\partial \tau}\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)-4\lambda^4\dot{x}^s\frac{\partial}{\partial x^s}\left(\frac{m_1}{r_1}\dot{\eta}^m+\frac{m_2}{r_2}\dot{\xi}^m\right)$$

$$+4\lambda^4\dot{x}^s\frac{\partial}{\partial x^m}\left(\frac{m_1}{r_1}\dot{\eta}^s+\frac{m_2}{r_2}\dot{\xi}^s\right)+0(\lambda^6); \tag{27}$$

$$\lambda^2\dot{x}^p\dot{x}^q\,\Gamma^m_{pq} = \lambda^2\dot{x}^p\dot{x}^q\cdot\tfrac{1}{2}g^{m\mu}\left[\frac{\partial h_{p\mu}}{\partial x^q}+\frac{\partial h_{q\mu}}{\partial x^p}-\frac{\partial h_{pq}}{\partial x^\mu}\right]$$

$$= 2\lambda^4\dot{x}^m\dot{x}^q\frac{\partial}{\partial x^q}\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)-\lambda^4\dot{x}^s\dot{x}^s\frac{\partial}{\partial x^m}\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)+0(\lambda^6). \tag{28}$$

$$-\tfrac{1}{2}\lambda^2\dot{x}^m\frac{d}{d\tau}\log\left[g_{oo}+2g_{no}\lambda\dot{x}_n+\lambda^2\dot{x}^p\dot{x}^q g_{pq}\right]$$

$$= -\tfrac{1}{2}\lambda^2\dot{x}^m\frac{d}{d\tau}\log(1+h_{oo}-\lambda^2\dot{x}^p\dot{x}^p)+0(\lambda^6)$$

$$= -\tfrac{1}{2}\lambda^4\dot{x}^m\frac{d}{d\tau}\left[-\frac{2m_1}{r_1}-\frac{2m_2}{r_2}-\dot{x}^p\dot{x}^p\right]+0(\lambda^6). \tag{29}$$

Making the necessary substitutions for the various terms in (19) we get

$$\lambda^2\left[\ddot{x}^m-\frac{\partial}{\partial x^m}\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)\right]$$

$$= \lambda^4\left\{\tfrac{1}{2}\frac{\partial}{\partial x^m}\left(m_1\frac{\partial^2 r_1}{\partial \tau^2}+m_2\frac{\partial^2 r^2}{\partial \tau^2}\right)-2\dot{x}^m\frac{\partial}{\partial \tau}\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)-\dot{x}^m\frac{d}{d\tau}\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)\right.$$

$$\left.-\dot{x}^m\dot{x}^s\ddot{x}^s+\dot{x}^s\left[4\dot{\eta}^m\frac{\partial}{\partial x^s}\left(\frac{m_1}{r_1}\right)+4\dot{\xi}^m\frac{\partial}{\partial x^s}\left(\frac{m_2}{r_2}\right)-2\dot{x}^m\frac{\partial}{\partial x^s}\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)\right]\right.$$

$$+4\,\dot{\eta}^m \frac{\partial}{\partial\tau}\left(\frac{m_1}{r_1}\right) + \frac{4\,m_1}{r_1}\,\ddot{\eta}^m + 4\,\dot{\xi}^m \frac{\partial}{\partial\tau}\left(\frac{m_2}{r_2}\right) + 4\,\frac{m_2}{r_2}\,\ddot{\xi}^m$$

$$+ \frac{\partial}{\partial x^m}\left[-2\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)^2 + \frac{m_1}{r_1}\left(\tfrac{3}{2}\,\dot{\eta}^s\dot{\eta}^s - \frac{m_2}{r_{12}}\right) + \frac{m_2}{r_2}\left(\tfrac{3}{2}\,\dot{\xi}^s\dot{\xi}^s - \frac{m_1}{r_{12}}\right)\right]$$

$$-4\,\dot{x}^s \frac{\partial}{\partial x^m}\left(\frac{m_1}{r_1}\,\dot{\eta}^s + \frac{m_2}{r_2}\,\dot{\xi}^s\right) + \dot{x}^s\dot{x}^s \frac{\partial}{\partial x^m}\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)\Big\} + 0\,(\lambda^6). \tag{30}$$

In simplifying (30) we note that

$$\frac{\partial r_1}{\partial\tau} = -\frac{\partial r_1}{\partial x^s}\,\dot{\eta}^s \tag{31}$$

$$\frac{\partial^2 r_1}{\partial\tau^2} = -\frac{\partial r_1}{\partial x^s}\,\ddot{\eta}^s + \frac{\partial^2 r_1}{\partial x^p\,\partial x^q}\,\dot{\eta}^p\dot{\eta}^q \tag{32}$$

$$\frac{\partial^2 r_2}{\partial\tau^2} = -\frac{\partial r_2}{\partial x^s}\,\ddot{\xi}^s + \frac{\partial^2 r_2}{\partial x^p\,\partial x^q}\,\dot{\xi}^p\dot{\xi}^q \tag{33}$$

$$\frac{\partial}{\partial\tau}\left(\frac{m_1}{r_1}\right) = \dot{\eta}^s \frac{\partial}{\partial\eta^s}\left(\frac{m_1}{r_1}\right) = -\,\dot{\eta}^s \frac{\partial}{\partial x^s}\left(\frac{m_1}{r_1}\right) \tag{34}$$

$$\frac{\partial}{\partial\tau}\left(\frac{m_2}{r_2}\right) = -\dot{\xi}^s \frac{\partial}{\partial x^s}\left(\frac{m_2}{r_2}\right) \tag{35}$$

$$\frac{d}{d\tau}\left(\frac{m_1}{r_1}\right) = (\dot{x}^s - \dot{\eta}^s)\frac{\partial}{\partial x^s}\left(\frac{m_1}{r_1}\right) \tag{36}$$

$$\frac{d}{d\tau}\left(\frac{m_2}{r_2}\right) = (\dot{x}^s - \dot{\xi}^s)\frac{\partial}{\partial x^s}\left(\frac{m_2}{r_2}\right) \tag{37}$$

$$\ddot{x}^s = \frac{\partial}{\partial x^s}\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right) + 0\,(\lambda^2) \tag{38}$$

$$\ddot{\eta}^s = \frac{\partial}{\partial x^s}\left(\frac{m_2}{r_{12}}\right) + 0\,(\lambda^2) \tag{39}$$

$$\ddot{\xi}^s = \frac{\partial}{\partial x^s}\left(\frac{m_1}{r_{12}}\right) + 0\,(\lambda^2). \tag{40}$$

So, on neglecting terms of the order of λ^6 we get from (30)

$$\lambda^2\left[\ddot{x}^m - \frac{\partial}{\partial x^m}\left(\frac{m_1}{r_1}+\frac{m_2}{r_2}\right)\right]$$

$$= \lambda^4\left\{\left[\dot{x}^s\dot{x}^s - 4\,\dot{x}^s\dot{\eta}^s + \tfrac{3}{2}\,\dot{\eta}^s\dot{\eta}^s - \frac{4\,m_1}{r_1} - \frac{4\,m_2}{r_2} - \frac{2\,m_2}{r_{12}}\right]\frac{\partial}{\partial x^m}\left(\frac{m_1}{r_1}\right)\right.$$

$$+ \left(\dot{x}^s\dot{x}^s - 4\,\dot{x}^s\dot{\xi}^s + \tfrac{3}{2}\,\dot{\xi}^s\dot{\xi}^s - \frac{4\,m_1}{r_1} - \frac{4\,m_2}{r_2} - \frac{2\,m_1}{r_{12}}\right]\frac{\partial}{\partial x^m}\left(\frac{m_2}{r_2}\right)$$

$$+ \left[4\,\dot{x}^s\,(\dot{\eta}^m - \dot{x}^m) + 3\,\dot{x}^m\dot{\eta}^s - 4\,\dot{\eta}^m\dot{\eta}^s\right]\frac{\partial}{\partial x^s}\left(\frac{m_1}{r_1}\right)$$

$$+[4\dot{x}^s(\dot{\xi}^m-\dot{x}^m)+3\dot{x}^m\dot{\xi}^s-4\dot{\xi}^m\dot{\xi}^s]\frac{\partial}{\partial x^s}\left(\frac{m_2}{r_2}\right)$$

$$+\frac{4m_1}{r_1}\frac{\partial}{\partial x^m}\left(\frac{m_2}{r_{12}}\right)+\frac{4m_2}{r_2}\frac{\partial}{\partial x^m}\left(\frac{m_1}{r_{12}}\right)-\tfrac{1}{2}m_1\left(\frac{\partial r_1}{\partial x^s}\right)\frac{\partial}{\partial x^s}\left(\frac{m_2}{r_{12}}\right)$$

$$-\tfrac{1}{2}m_2\left(\frac{\partial r_2}{\partial x^s}\right)\frac{\partial}{\partial x^s}\left(\frac{m_1}{r_{12}}\right)$$

$$+\tfrac{1}{2}m_1\frac{\partial^3 r_1}{\partial x^m\,\partial x^p\,\partial x^q}\dot{\eta}^p\dot{\eta}^q+\tfrac{1}{2}m_2\frac{\partial^3 r_2}{\partial x^m\,\partial x^p\,\partial x^q}\dot{\xi}^p\dot{\xi}^q\Big\}. \tag{41}$$

If by changing the density of the first body we can make approximately,

$$m_1=0,\ m_1/r_1=0,\ \partial/\partial x^m\,(m_1/r_1)=0 \tag{42}$$

we have

$$r_2=r_{12} \tag{43}$$

and (41) reduces to

$$\ddot{x}^m-\frac{\partial}{\partial x^m}\left(\frac{m_2}{r_{12}}\right)=\lambda^4 m_2\Big\{\Big[\dot{x}^s\dot{x}^s+\tfrac{3}{2}\dot{\xi}^s\dot{\xi}^s-4\dot{x}^s\dot{\xi}^s-\frac{4m_2}{r_2}\Big]\frac{\partial}{\partial x^m}\left(\frac{1}{r_{12}}\right)$$

$$+[4\dot{x}^s(\dot{\xi}^m-\dot{x}^m)+3\dot{x}^m\dot{\xi}^s-4\dot{\xi}^m\dot{\xi}^s]\frac{\partial}{\partial x^s}\left(\frac{1}{r_{12}}\right)$$

$$+\tfrac{1}{2}\frac{\partial^3 r_{12}}{\partial x^m\,\partial x^p\,\partial x^q}\dot{\xi}^p\dot{\xi}^q\Big\}. \tag{44}$$

This is precisely what (17) reduces to when $m_1=0$. Hence the consistency of the new method with the geodesic postulate is established as far as this test goes. We could have tested the consistency further by comparing (41) itself with the form of equations for m_3 in the field of m_1 and m_2, as given by the new method, when m_3 is negligible. E.I.H. does not given the three-body equations and we have therefore to be content with the comparison afforded by the two-body problem. As far as our calculations of the three-body problem go (41) is found to be consistent with the corresponding form of Einstein's equations of motion.

§ 4. We will now proceed to consider how it is possible to reconcile the equations of motion obtained from

$$G_{\mu\nu}=0$$

with the geodesic postulate. The clue is provided by the identities,

$$(G^{\mu\nu}=\tfrac{1}{2}G\,g^{\mu\nu})_\nu=0. \tag{45}$$

Certain functions $\overset{k}{C}_m(\tau)$ which enter the method of E.I.H. have the property that when all $\overset{k}{C}_m\to 0$, $G_{\mu\nu}$ also tends to zero. If $\overset{k}{C}_m\neq 0$ for one value of m or k, $G_{\mu\nu}\neq 0$ also. Now

$$\overset{k}{C}_m=0 \qquad m=1,2,3 \tag{46}$$

are the equations of motion of the kth particle of the system in Einstein's method. Let us see how $G_{\mu\nu}$ can be made to tend to zero so that when the mass of the kth particle is zero (46) is consistent with the equations of geodesics. When $G_{\mu\nu} \neq 0$ its value can be expressed in the normal form:

$$G_{\mu\nu} = \rho_0 u_\mu u_\nu - \rho_1 v_\mu v_\nu - \rho_2 w_\mu w_\nu - \rho_3 x_\mu x_\nu, \tag{47}$$

where u_μ is a timelike unit vector and v_μ, w_μ and x_μ are spacelike unit vectors. Also

$$G = \rho_0 + \rho_1 + \rho_2 + \rho_3 \tag{48}$$

and

$$g_{\mu\nu} = u_\mu u_\nu - (v_\mu v_\nu + w_\mu w_\nu + x_\mu x_\nu). \tag{49}$$

The identities (45) now become

$$\{(\rho_0 - \rho_1 - \rho_2 - \rho_3)\, u^\mu u^\nu + (\rho_0 - \rho_1 + \rho_2 + \rho_3)\, v^\mu v^\nu + (\rho_0 + \rho_1 - \rho_2 + \rho_3)\, w^\mu w^\nu + (\rho_0 + \rho_1 + \rho_2 - \rho_3)\, x^\mu x^\nu)\}_\nu = 0. \tag{50}$$

$$G_{\mu\nu} \to 0 \qquad \text{as } \rho_\mu \to 0. \tag{51}$$

Hence (50) will reduce to the equations of a geodesic,

$$(u^\nu)_\nu\, u^\nu = 0$$

when along with $\rho_\mu \to 0$ we have also

$$\frac{\{(\rho_0 - \rho_1 + \rho_2 + \rho_3) v^\mu v^\nu + (\rho_0 + \rho_1 - \rho_2 + \rho_3) w^\mu w^\nu + (\rho_0 + \rho_1 + \rho_2 - \rho_3) x^\mu x^\nu\}_\nu}{\{(\rho_0 - \rho_1 - \rho_2 - \rho_3) u^\nu\}_\nu} \to 0. \tag{52}$$

It is not necessary that the conditions (52) will always be satisfied. It is the special virtue of Einstein's method that (52) is satisfied at least upto 0 (λ^6). Herein lies an explanation of the consistency with the geodesic postulate as discovered by us. Incidentally it is of some astronomical interest to observe that if the bodies of masses m_1 and m_2 are looked upon as the earth and the sun the equation (41) obtained by us gives the motion of the moon in the field of the others.

Summary

We derive an equation (41) for the geodesics in the field of two bodies as given by Einstein, Infeld and Hoffmann. It is shown that when $m_1 = 0$ the equation reduces to that of the two-body problem (17) obtained without any reference to the geodesic postulate. This is the main result of the paper. Although Einstein's new method of deriving gravitational equations of motion is based on the field equations only we show how it can be consistent with the geodesic postulate if the field tensor tends to zero in a particular manner.

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THE EFFECT OF SUNSET ON ATMOSPHERICS

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Introduction

In recent years the study of atmospherics has been made from several points of view. The credit for starting a systematic study goes to Appleton, Watson and Watt (1923), who during their early researches recorded the wave forms of atmospherics with a cathode-ray oscillograph and classified them into aperiodic, periodic and quasi-periodic types. It was also found that in many cases, the main structure of the atmospheric was supplemented by ripples of short duration.

Atmospherics and Lightning.

A study of lightning and its relationship to atmospherics has been made in great detail by several observers. Besides studying the wave forms of atmospherics, Watt and Appleton have analysed some 15,000 directional bearings and located the regions from which atmospherics originate. They found that 94% of the atmospherics could directly be associated with contemporary rainfall areas, 35% located in front of cyclonic depressions and 15% with thunder and lightning. At about the same time, a detailed study of the sudden changes in the electric field accompanying a lightning flash was carried out by Appleton, Watt and Herd (1926). It was found that lightning discharges are capable of producing radiation fields similar in wave form and magnitudes to those of atmospherics of distant origin.

Schonland and Collens (1933), from a study of the photographs of 50 separate lightning discharges from two thunderstorms, with the Boys' rotating lens camera, found that many apparently continuous discharges are made up of a number of discrete strokes varying in number from 1 to 12 separated by short periods. The majority of the strokes were found to be double and to consist of a dart-like, downward-moving leader stroke, followed immediately on arrival at the ground by a more intense flame-like, upward-moving main stroke. It was further found that the duration of a complete lightning flash is often of the order of 1 second, although later observers give much longer periods. Malan and Collens (1935) showed that each of these

strokes is composite consisting of a leader portion and the main stroke. The leader to the first stroke consists of a series of streamers moving in a step by step manner (stepped leader).

Appleton, Watson, Watt and Herd (1926) and Cairns (1927) and others who studied atmospherics with the aid of cathode-ray oscillographs give times of the order of milliseconds for the duration of atmospherics, while observations made in Australia, using an ordinary tuned receiving set and recording the motion of the string of an Einthoven galvanometer on moving photographic paper, have given durations ranging in most cases from ·2 to ·5 seconds. Munro and Webster (1934) examined the wave form of atmospherics with an aperiodic receiver and a cathode-ray oscillograph with a time base of slower period (·1 second) and found that an atmospheric really consists of a number of discrete pulses separated by clear intervals. The sizes and separations of the component pulses were found to vary in an irregular manner and thus to give rise to the rough noises produced in a broadcast receiver.

The observations of Appleton, Watt and Herd were evidently made with such rapid time bases that only one of the constituent pulses was observed on each occasion. With a tuned receiving set, and reading with a galvanometer with a relatively long period, the constituent parts of an atmospheric are merged together and the duration recorded is that of the whole succession of pulses, *i.e.*, the duration as it would appear to a broadcast listener.

It was pointed out by the author (1935), as a result of preliminary investigations on atmospherics carried out with the aid of a receiver tuned to a wavelength of 400 metres and a galvanometer of period 1 second, that the records show certain thickenings (Fig. 1) along the trace of the galvanometer motion. The number of thickenings indicates the number of separate impulses received by the galvanometer in any given interval, and these could be arranged into groups taking into consideration the rate at which they succeed each other. From Fig. 1 which is an enlargement of a section of one of the records it can easily be seen that the total duration of each atmospheric appears to be about 1/2 second, and the photographs show that the atmospherics recorded have a number of components ranging from 4 to 12. Each of these constituent impulses may have a fine structure, which cannot be revealed except when examined with a cathode-ray oscillograph. The dots may be considered as indicating the gross structure of an atmospheric and may be directly traced to the constituent strokes of a lightning discharge.

Norinder (1936) from simultaneous observations of atmospherics with the aid of loud speakers of radio receiving sets and corresponding records

with cathode-ray oscillographs, found two characteristic forms of atmospherics in connection with thunderstorms : (1) the ' clicks ' singular, discharges of a comparatively short period (up to 100 milliseconds) caused apparently by very short discharges within adjacent parts of a thundercloud ; and (2) the ' grinders ' consisting of repeated swarms of field variations extended over long intervals of time (200 to 400 milliseconds and in some cases even from 3000 to 4000 milliseconds) and caused by distant lightning discharges. Appleton, Watt and Herd (1926) pointed out that the individual atmospheric wave forms were either of an aperiodic or quasi-periodic electric disturbance of duration 2–3 milliseconds. High frequency ripples on the main gross structure were also observed and the interferent effects of atmospherics were attributed to such high frequency components rather than to the effect of the relatively slow main disturbance.

Appleton and Chapman (1937), by studying atmospherics of known (thunderstorm) origin, with improved apparatus, have given a more satisfactory account of the high frequency components and a complete picture of the evolution of the atmospheric from the original disturbance and also a detailed description of the remarkable sequence of alterations of wave form with distance. The analysis of radiation fields of atmospherics showed that the most frequent type is one with a single component, but after this the number of components 2 or 3, 4 or 5, occur with decreasing frequency. The analysis of some thousands of records of the nett field changes due to lightning, with the aid of a string electrometer and later with a cathode-ray oscillograph, also showed that the most frequent type of discharge is one that takes place in a single step, but that the next most frequent number of steps is either two or three, double or triple discharges being equally frequent. Further the records show tendency for the atmospheric to occur in groups corresponding to the time sequence of partial discharges of varying intensity.

It was also shown that with increasing distance the total duration of atmospherics appears to increase, the wave form becoming more regular and the high frequency ripples less prominent. At a distance of about 200 kilometers the wave form of the atmospheric disturbance is determined practically entirely by the radiation field of the discharge. At still greater distances a slow tail of about two rounded half cycles developed.

Atmospherics and Thunderstorms.

In all the above investigations an attempt has been made to study the wave form, duration and its variations with distance of atmospherics and to correlate it with the detailed studies of lightning as the source of atmospherics. Lightning has its origin in the existence in the lower atmosphere of certain

special type of meteorological conditions. There is no lack of evidence that we must look to thunderstorms upto very considerable distances as important sources of atmospherics. A thunderstorm from the point of view of a meteorologist is defined as a procedure in the atmosphere which is connected with disruptive discharges that ought to be visible or audible or both. For their development, such discharges require charge accumulations and field forces along the discharge region, of dimensions which we are not yet able to reproduce in the laboratory. These accumulations of charges and the building up of strong fields are thus defined as a thunderstorm when lightning has occurred within the active regions of the atmosphere.

Observations on atmospherics with a narrow sector directional recorder by Munro, Wark and Higgins (1936) point to two main types of sources, which they classify as regular and irregular. The regular ones are tropical thunderstorm areas and the irregular ones of lower activity are chiefly 'frontal' thunderstorms, associated with cold fronts. These authors consider atmospherics as valuable in weather forecasting.

Several attempts made to correlate the occurrence of atmospherics with weather conditions, to locate storm and thunderstorm areas with the aid of atmospherics have yielded very valuable information. A large amount of work has been done by R. Bureau and others (1926) who have reached the conclusion that atmospherics are the phenomena that best give evidence of the passing of a meteorological disturbance in tropical regions. The other meteorological variables only indicate that passing in a much less regular manner. Moreover they only give evidence of the meteorological disturbance when it has reached the observing station while atmospherics announce it some hours in advance.

It is now generally agreed that the majority of atmospherics encountered in radio communication originate in lightning flashes, and the prominent source of the world's supply at any hour lies in a land where it is summer afternoon (Watt, 1929) and India being one of the chief sources of atmospherics affords ample scope for study.

A study of atmospherics especially of their relationship with meteorological conditions has been made by me for sometime past. Prior to these investigations I had noticed that at certain times of the year atmospheric disturbances were more intense on short waves than on the medium waves, although, as a general rule, atmospheric activity is very much greater on the medium waves, and further that the periods of maximum activity on the short waves did not always coincide with similar periods on the medium waves. It was therefore expected that a study of these differences might

give a clue to the identification of particular types of disturbances with definite types of meteorological conditions.

Experiment

General Plan of Experiment.

It therefore became necessary to take simultaneous records of atmospherics on two wavelengths, one in the medium wave band and another in the short wave band. In order to determine the diurnal variation of atmospherics, the study had to be carried out throughout the day. Continuous recording and the use of high speed recorders like the cathode-ray oscillograph were entirely out of the question on account of the high cost involved. Moreover the cathode-ray oscillograph is useful for the study of fine structure of atmospherics over short intervals of time and not well suited for the observations required in the present investigation. It was, therefore, decided that the study should be carried out with the aid of cheap and simple apparatus. Two radio receivers, each tuned to one of the chosen wavelengths together with a moving coil galvanometer having a comparatively large period (about 2 seconds) were employed, and the motion of the two spots of light reflected from the mirrors of the galvanometers were recorded photographically on bromide paper wound round a rotating drum.

In the place of continuous recording for all the 24 hours in the day, it was decided that sample records should be taken for about two minutes at intervals of one hour throughout the day. The two minute records were, from previous observations made by the author (1935), found to be sufficiently representative of the atmospheric activity at that period. An automatic device, details of which are given later, was constructed and used for making these records. With its aid, the two wireless receivers, the two galvanometer lamps and the motor used for rotating the drum were switched on at intervals of one hour. Records were then taken for about 2 minutes and the entire apparatus was switched off. This procedure was repeated throughout the day. Bromide paper of size $10'' \times 12''$ was employed, one half of it being used for the medium wave records and the other for the short wave records. A sample record is given in Fig. 2. The records, as explained earlier (Subba Rao,1935) give information regarding the gross structure of the atmospheric and it is possible with their aid to identify the types of atmospherics described as ' clicks ' and ' grinders ' and to count the number of constituent impulses that make up any of the recorded atmospherics. These details are clearly visible in the enlargement of a small portion of one of the records (Fig. 1) taken during the preliminary work.

In the course of this work on atmospherics a striking feature was noticed. Atmospheric activity showed sudden increase after sunset. To determine the precise nature of the effect of sunset, the records taken over a fortnight from 14th to 28th of August 1940, were analysed in detail. The present paper discusses the results of this analysis. This particular period was chosen because atmospheric activity is generally very much lower than in summer, and the variation in atmospheric activity may be more clearly observed and their relationships to meteorological conditions more definitely established.

Apparatus.

The apparatus used in this investigation consists of two Pye 803 5-valve superhets with the AVC circuits put out of action. One of these was tuned to a wavelength of 375 metres and the other to 37·5 metres. Care was taken to see that there was no wireless station operating on these wavelengths. The outputs of these receivers were shunted on to two moving coil galvanometers having periods of about 2 seconds. As the atmospheric activity on medium waves was always greater than that on the short waves, only a fraction, approximately, 1/6 (4/25) of the output of the first receiver is connected to the galvanometer. The galvanometers were sufficiently damped so that when the coils were displaced they returned to rest always before the completion of one oscillation. This was found to be essential in order to prevent the free oscillations of the galvanometer from interfering with the records of atmospherics.

The rotating drum was driven by an electric motor geared down to the requisite speed. After trying various speeds it was found that a speed corresponding to a traverse of the spot of light of 4½″ per minute was found to be quite adequate for the purpose.

Estimates of the intensities of atmospherics were made from the records on a scale of 5. When the atmospherics come in groups following each other in quick succession it is not possible to estimate the strength of the individual components of the groups and in such cases the throw of the galvanometer has been taken as representing the intensity of the group. The number of components in any group could easily be counted from the records as each individual component of the atmospheric produces a slight thickening of the curve at the instant when it arrives as can be seen from Fig. 1.

Automatic Switching.

The automatic switching was carried out with the aid of an ordinary clock regulated to keep correct time; a small circular ebonite disc (1·5 cm. in diameter and 4 mm. thick) was attached to the minute hand spindle. A strip

of brass A is embedded on the circumference of this disc and this strip is electrically connected to the spindle and through it to the body of the clock. Pressing against this disc is another strip of brass B insulated from the body. By means of the spring C the pressure of the strip B on the disc is maintained constant.

The body of the clock and the insulated strip are connected to two binding screws, H and K, to the ends of which the electrical circuit shown in the diagram is connected. The circuit consists of 6 Leclanche cells in series with an electromagnet. When the strip comes in contact with A, the electric circuit is closed and the magnet is energised. The position of the disc on the spindle is adjusted so that A comes into contact with B when the minute hand is at 60. Thus this relay circuit is closed automatically at intervals of one hour. The period for which the circuit is closed depends on the width of the brass piece A. In the present arrangement it has been adjusted to a period of about 3 minutes. The attachment of this device does not in any manner interfere with the normal working of the clock.

The energised electromagnet is made to close the main switch S, shown in Fig. 3. A lever about 25 cm. long is pivoted at O from an upright pillar. S is a spring whose tension can be adjusted with the aid of a screw. I is a soft iron piece carried by the lever above the poles of the electromagnet. The distance of this piece from the poles of the electromagnet can be altered by means of a screw not shown in the figure. At the free end of this rod, horizontally and at right angles to it, is fixed an ebonite strip which carries at its ends a thick copper rod R bent into the form indicated. When the electromagnet is energised, the rod is pulled down and closes the mercury switch S_1 which consists of the two cups 1 cm. deep scooped out of ebonite and three-fourths full of mercury. These two mercury cups were connected in series with the mains 220 volts A.C. 50 cycles. To prevent sparking a suitable condenser is connected across these terminals.

As the receivers used in the present experiment were mains operated, with indirectly heated valves an interval of about 1 minute was required for heating the valves and bringing the sets into operation. The galvanometer lamps and the motor for rotating the drum had to be switched on only after the lapse of this interval. This delay was brought about by the introduction of a bimetal strip of brass and iron over which nichrome wire 26 s.w.g. was wound, necessary insulation being provided with the aid of thin mica sheets.

With the aid of a rheostat in series with the nichrome wire, the current through it could be regulated. This circuit is connected in parallel with the wireless receivers and is closed by the switch S_1. While the valves are getting

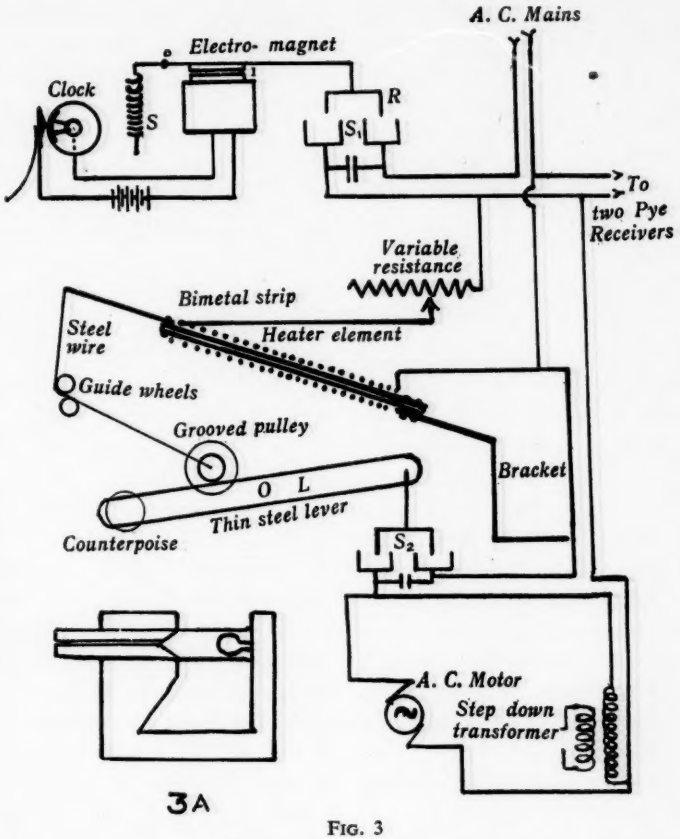

FIG. 3

heated, the bimetal strip bends downwards and closes and the other main Switch S_2 through the lever L. The Switch S_2 closes the circuit of (1) the motor geared down to the required speed for rotating the drum and that of (2) the primary of a filament transformer (230 V to 4 V). Across the secondary of this transformer are connected two flash light lamps (3·5 V) with spherical bulbs and each of these is fitted at one end of a narrow tube of brass (15 cm. long and 1 cm. in diameter as shown in Fig. 3A). To the other end of the tube is fitted a cap with a narrow circular slit. With the aid of this arrangement a narrow beam of light along the axis of the brass tubes is obtained and this in conjunction with the galvanometer mirror is employed for photographic registration. The image of the spot of light was finally sharply focussed on the drum with the aid of a convex lens ($f = 10$ cm.).

Thus the recording apparatus was put into operation only about a minute after the receivers were switched on. The total duration for which the main switch S_1 is kept closed is 3 minutes and is controlled by the clock. The time for which the record is taken is equal to the difference between the duration for which S_1 is closed and the time taken by the bimetal strip to close S_2. Thus keeping the total duration constant, the duration of the records can be altered at will with the aid of the rheostat.

In order to prevent arcing it was necessary to make the bimetal strip operate S_2 quickly. This was made possible by using a bimetal strip 10″ long and attaching to its end a brass rod 4″ long. This rod has to close S_2 at the end of one minute and to keep it closed for a period of about 2 minutes. During this two minutes interval, the heater current is still on and there is a progressive bending of the bimetal strip which means that sufficient clearance has to be provided for the bending of the strip even after the contact with the mercury cups of switch S_2 is made. This led to several mechanical difficulties which were finally solved by the design of the apparatus indicated in Fig. 3. A steel wire joined to the end of the brass rod after passing over two guide wheels was attached to a heavy brass grooved pulley running on a flat steel strip. This strip was pivoted at its centre and its equilibrium is suddenly upset, when the grooved pulley goes beyond a particular position. When this happens the switch S_2 is suddenly closed. Further bending of the metal strip only pushes the grooved pulley to the right but that does not introduce any mechanical difficulties. When S_1 is broken by the clock the current through the heater is switched off and the bimetal strip, the lever and the grooved pulley regain their original positions slowly and the above process is repeated every hour. The time taken by the bimetal strip to cool is about 8 minutes.

The Records.

A sample record is given in Fig. 2. Only those atmospherics recorded on the medium waves from 9 hours on the 17th August 1940 to 13 hours on the 18th August 1940 are shown. This includes the period represented by curve 9*a*. The hours at which the records are taken are marked on the record. A look at the plate gives a rough idea of how atmospheric activity varies from hour to hour.

As pointed out in an earlier paper (Subba Rao, 1935) the kick of the galvanometer has been taken as a measure of the intensity of the atmospherics and the number of atmospherics (or atmospheric groups) reaching the observer in one minute could easily be counted. Although it was found convenient to plot the variations in the number of atmospherics received

per minute and in the intensity in the earlier investigation, a different procedure was adopted for the graphical representation of the results of the present investigation. The sum of all the impulses received by each one of the galvanometers during one minute has been taken as the measure of atmospheric activity and this quantity is shown on the Y-axis in the various graphs.

Records of the Atmospherics between the 14*th and* 28*th August* 1940.

The ordinates indicate the times of the day at which the observations were made and the abscissæ the corresponding activity. The time corresponding to sunset is indicated by the thick dark line parallel to the Y-axis. The time of sunset varied from 18 hours 30 minutes on the 14th to 18 hours 22 minutes on the 28th. As it is not possible to indicate these slight variations on the graph, this line is drawn at 18 hours 24 minutes for the sake of convenience.

The thick line indicates activity on the medium waves and the thin line that on the short waves. The scales marked are common to both the graphs. It is however to be remembered that the curves do not represent relative activities on the medium and short waves as only a small portion (1/6) of the output of the receiver is coupled to the galvanometer in the first case and the entire amount in the other. Since the object of these preliminary investigations was to study how the activities on the two wavelengths respectively vary from hour to hour, the plots of the indications of the galvanometers were considered quite adequate for the purpose and no attempt has been made to reduce them to a common scale of measurement.

Results

As the activity of the medium waves forms the main subject of the study, the various records may be grouped as detailed below according to the effects observed on the medium waves before and after sunset.

Group 1.—Records in which atmospheric activity is practically nil before sunset, *i.e.*, (at 18 hours) and rises very rapidly after sunset (at 19 hours).

Group 2.—Records with zero activity before sunset ; with slight rise after sunset; showing increase by larger steps later.

Group 3.—Those showing activity even before sunset and slight increase of activity after sunset.

Group 4.—Those showing activity even before sunset but with a fall in activity after sunset.

Data relating to these records are abstracted in Table I.

TABLE I

Group	Curve No.	Date	Activity on medium wave at	
			18 hours	19 hours
I (Fig. 4)	1*a*	20-8-40	5	80
	2*a*	21-8-40	0	69
	3*a*	23-8-40	0	51
II (Fig. 5)	4*a*	18-8-40	4	19
	5*a*	19-8-40	0	12
	6*a*	22-8-40	0	15
	7*a*	24-8-40	0	13
III (Fig. 6)	8*a*	14-8-40	10	13
	9*a*	17-8-40	25	45
IV (Fig. 6)	10*a*	15-8-40	44	37
	11*a*	16-8-40	32	30

The first column indicates the group into which the particular record is placed. The second indicates the serial number of the curves in Figs. 4, 5 and 6. The third column gives the date on which the effect of sunset is discussed. In the 4th and 5th columns are given the measures of total activity on the medium waves computed from the records of atmospherics as described earlier, at 18 hours and 19 hours. The sun sets at 18 hours 24 minutes.

The Characteristic Features of the Effect of Sunset on the Members of the Various Groups.

Group 1.—This group consists of the records of atmospherics on the 20th, 21st and the 23rd August respectively. As indicated by the curves in Fig. 4 the activity at 18 hours is zero, on the 21st and 23rd and practically zero (actually 5) on the 20th. It will be noticed that starting with practically zero activity before sunset, the activity rises to very large values, 80, 69 and 51 respectively on the three days at 19 hours.

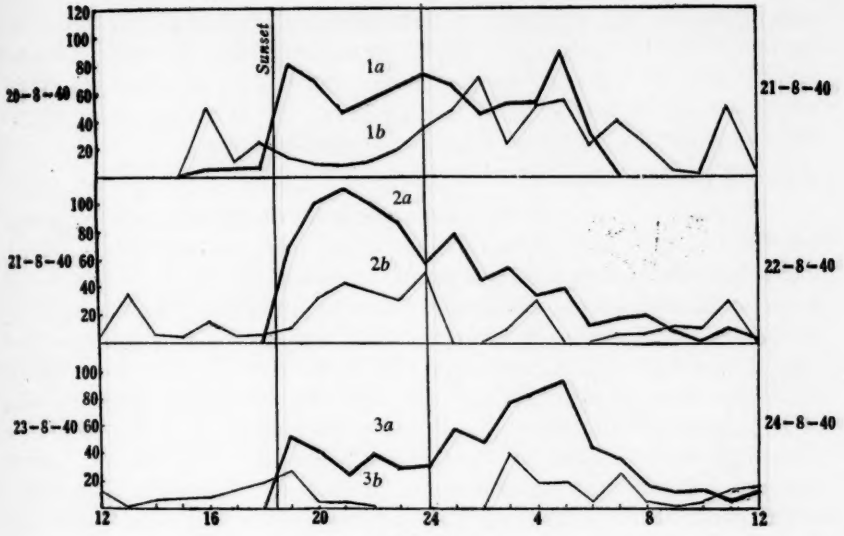

FIG. 4

The Trigger Action.

This sudden increase in activity within about half an hour after sunset reminds one of the *Trigger Action in the Atmosphere* described by Napier Shaw (1933). According to him two conditions have to be satisfied in order that a display of energy may occur automatically in the atmosphere. This display takes the form of a thunderstorm. The first condition to be satisfied is the existence of a state of liability in the atmosphere caused by the establishment of a thick layer in convective equilibrium. This is brought about by the heating effect of solar radiation on land. The other is the provision at the right moment of a sufficient quantity of air saturated with water vapour which is again brought about by the effect of solar radiation on water. The combination of these two is not more usual than a violent thunderstorm which is in many ways suggestive of trigger action.

When the thunderstorm commences atmospheric activity also commences and the measure of atmospheric activity will indicate the violence of the thunderstorm. From the data given in Table I, it is clear that the atmospheric or thunderstorm activity commences only after sunset and therefore it is very likely that it is the removal of solar radiation that operates the trigger. It is also reasonable to assume that there were in existence even before sunset conditions favourable for the starting of thunderstorm activity, the occurrence of lightning and the generation of atmospherics, but that the presence of

solar radiation was exercising a restraining influence thus preventing the starting of the thunderstorm. When the sun sets, this influence is removed and the thunderstorm activity commences and quickly attains large magnitudes even within the period of half an hour. On this view, therefore, the effect of sunset may aptly be described as trigger action.

Effect of Sunset.

Although it is not possible to say exactly how solar radiation is responsible for the restraining influence, the studies of Schonland (1932) indicate that it is to the ionising influence of solar radiation that we must look for an explanation. Schonland has shown that a single lightning flash may easily discharge a cloud completely and that a fairly active cloud produces one flash every 20 seconds; which means that the cloud takes 20 seconds to recover its original state of electrification. He further finds that the recovery takes place so rapidly at the start, that if this rate continued, it would be able to restore the whole electrification in about 5 seconds. The recovery curve, however, is found to be exponential and this suggests that the initial rate may remain constant, but that, as the cloud charges grow, effects occur which tend to dissipate them and which are proportional to the quantity of charge present at any time. Thus at the moment just before a discharge most of the power of the machine is being expended in overcoming various leakage effects.

On the above view it is quite easy to explain the restraining influence of solar radiation on thunderstorm activity and the generation of atmospherics. Solar radiation tends to produce a state of ionisation in the atmosphere and this state greatly augments the leakage effects referred to above. Under the action of the greater leakage effects, it may happen that the field in the cloud never reaches the sparking value as long as the ionising influence of solar radiation is present. With the setting of the sun this influence is removed, the trigger is pulled and the electrostatic field builds up quickly and lightning flashes occur and the regular thunderstorm commences.

Group 2.—There are four records in Group 2. Here also the trigger action is quite evident although the activity at 7 (19 hours) is very much smaller than in records in Group 1. It can easily be seen from the curves (Fig. 5) that the activity reaches quite large values, not soon after sunset, but a few hours later.

Groups 3 and 4.—These consist of 2 curves each (Fig. 6). Activity before sunset is common to all these days but the sunset has affected them differently. On the 14th and 17th the trigger action of sunset is still evident although it is not so pronounced as in the records in the previous groups.

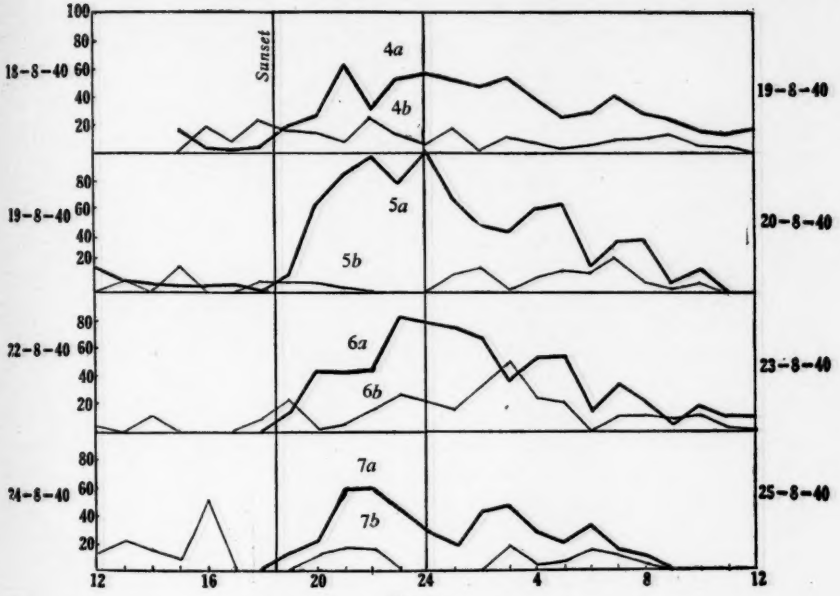
Sunset
4a
4b
5a
5b
6a
6b
7a
7b
18-8-40
19-8-40
22-8-40
24-8-40
19-8-40
20-8-40
23-8-40
25-8-40
100
80
60
40
20
12
16
20
24
4
8
12

FIG. 5

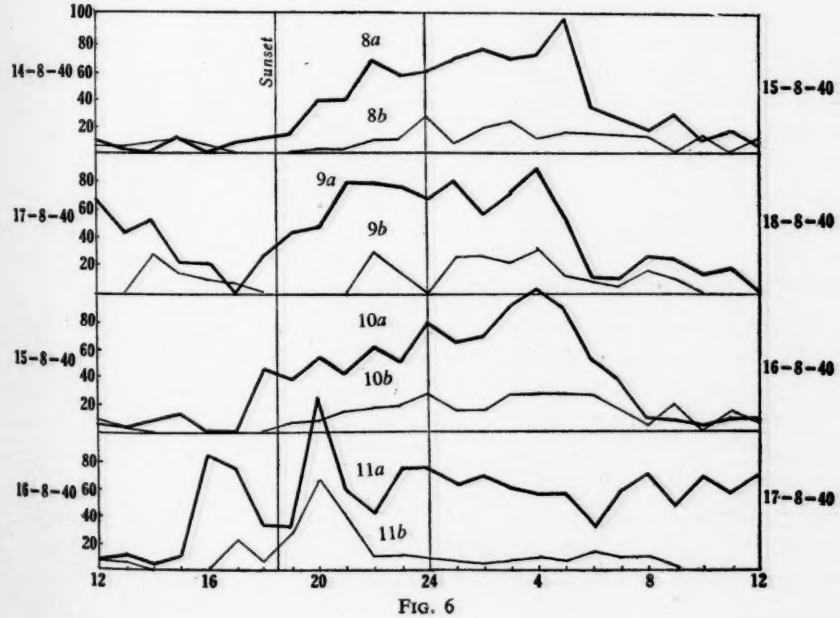
Sunset
8a
8b
9a
9b
10a
10b
11a
11b
14-8-40
17-8-40
15-8-40
16-8-40
15-8-40
18-8-40
16-8-40
17-8-40
100
80
60
40
20
12
16
20
24
4
8
12

FIG. 6

On the 15th sunset brings about a reduction in activity, while on the 16th there is practically no change. These two records therefore do not seem to indicate the normal effect of sunset which brings about an increase in atmospheric activity.

Analysis of Atmospherics according to Intensity.

This apparent discrepancy disappears when we consider the records from a different point of view. The activity on the various days at the specified times is due to a certain number of atmospherics. All of them naturally are not of the same intensity. If we examine the distribution of the number of atmospherics according to their intensities we obtain an insight into the actual mechanism of the effect of sunset on atmospherics. Such an analysis is given in Table II.

TABLE II

Classification of Atmospherics according to their Intensities

Group	Curve No.	Date	Hour	No. of atmospherics of intensities				No. of Atm./min.	Atmospheric activity
				2	3	4	5		
I	1*a*	20	18	1	1			2	5
			19	12	8	8		28	80
			20	7	9	7		23	69
	2*a*	21	18						
			19	12	11	3		26	69
			20	5	13	9	3	30	100
			21	4	9	8	9	30	112
	3*a*	23	18						
			19	15	3	3		21	51
			20	9	2	4		15	40
II	4*a*	18	18	2				2	4
			19	5	3			8	19
			20	5	3	2		10	27
			21	9	4	7	1	21	63
	5*a*	19	18						
			19	3	2			5	12
			20	5	9	6		20	61
			21	4	11	9	1 (6)	25	83
			22	6	6	14	2	28	96
	6*a*	22	18						
			19	4	1	1		6	15
			20	2	8	4		14	44
	7*a*	24	18						
			19	5	1			6	13
			20	5	4			9	22
			21	9	8	4		21	58
			22	7	11	3		21	59
III	8*a*	14	18	1	0	2		3	10
			19	5	1			6	13
			20	10	3	2		15	37
			21	6	6	2		14	38
	9*a*	17	18		3	4		7	25
			19	6	2	6		14	45
			20	7	1	7		15	45
			21	2	11	10		23	77

The first column gives the date of the record, the second, the hour at which the observations have been made. In the next four columns are indicated the number of atmospherics of intensities 2, 3, 4 and 5 respectively received during a total period of one minute. The next two columns indicate the total number of atmospherics received in one minute which is simply the total of the numbers in the previous four columns. The last column gives the total atmospheric activity which may be derived from the 3rd, 4th, 5th and 6th columns in the following way. Taking for example the observations on the 18th at 20 hours, there are 5 strokes of intensity 2; 3 of intensity 3 and 2 of intensity 4. The total number of atmospherics received per minute therefore is $= 5 + 3 + 2 = 10$. The activity which has been defined earlier as the sum of the intensities of all the atmospherics received in a minute equals $(5 \times 2) + (3 \times 3) + (2 \times 4) = 27$. These numbers 10 and 27 are entered in columns 7 and 8 respectively.

General Characteristics.

An examination of Table II brings out certain definite characteristics.

1. *Trigger Action.*—The effect of sunset is in all cases to bring about an increase in the number of atmospherics received per minute as well as in the total atmospheric activity. This is clearly indicative of the trigger action referred to earlier. The increase is observed to be very great on those days included in Group 1, less for those in Group 2 and very small for those in Group 3. In the cases included under Group 4 there is slight decrease, which means that the effect of sunset appears to bring about a decrease in atmospheric activity.

2. *The Progress of a Thunderstorm.*—It will also be noticed that at the commencement of the storm initiated by sunset a number of atmospherics of low intensities (2 and 3) are observed. It is therefore quite reasonable to assume that lightning flashes are of small magnitudes and they are probably flashes which it is not easy to observe from the ground. In some cases atmospherics of low intensities are accompanied by atmospherics of larger intensities also; but generally the atmospherics of small intensities are more numerous than those of large intensities. With the progress of the thunderstorm there come into existence relatively more and more atmospherics of larger intensities, while those of smaller intensities become relatively few. This is very strikingly illustrated by the data included under Group 1. Curves 1, 2, 3 and 9 show that in these cases there are a considerable number of atmospherics of larger intensities even at 19 hours. The presence of atmospherics of large intensities even at 19 hours, about half an hour after sunset, is indicative of the existence of a special set of conditions in the atmosphere; and it seems to

be connected with the sudden rise in atmospheric activity between 18 and 19 hours which is characteristic of the members of this group. These special features are discussed in detail later. When the thunderstorm has commenced, its progress takes place in the manner described above. There is an increasingly greater number of atmospherics of large intensities with a corresponding diminution of those of smaller intensities.

This appears to be the normal method of development of a thunderstorm or atmospheric activity, *i.e.*, commencing with a large percentage of atmospherics of low intensities, the emphasis shifts to those of large intensities. In all the above-mentioned cases the initiation of the storm is by the setting of the sun. It will be interesting therefore to consider the progress of a thunderstorm which takes place during the day. Such an example is afforded by the activity on the 16th. There was severe thunderstorm activity between 15 and 18 hours on this day. The analysis of the number of atmospherics according to intensities between 15 and 24 hours is given in Table III.

TABLE III

Classification according to Intensities of Atmospherics between 15 *and* 22 *Hours on the* 16*th August* 1940

Section	Hour	No. of atmospherics of intensities				Total No.	Total activity
		2	3	4	5 and above		
I	15	1	1	2		4	13
	16	5	20	3		28	82
	17		9	12		21	75
	18	1	6	3		10	32
II	19		6	3		9	30
	20		8	22	1, 1 (7)	32	124
	21	2	6	9		17	58
	22	4	7	3		14	41

The data may be divided into two sections. The first section refers to the period 15–18 hours. As indicated by curve 4 in Fig. 5 this corresponds to the evolution of the peak activity of 82 at 16 hours; at 16 hours the main body of atmospherics are of intensity 3; at 17 hours they are distributed among intensities 3 and 4 in the ratio of 9 : 12; at 18 hours, it is to be noted

that the main body of atmospherics has again shifted to lower intensities. By 18 hours the atmospheric activity has come down from 73 to 32.

The second section refers to the period 19–22 hours. This corresponds to the development of the peak activity of 124 at 20 hours. Here again it is noticed that nearly 2/3 or 67% of the atmospherics are confined to intensity 3. While at 20 hours 70% are of intensity 4; at this time there have also developed atmospherics of intensities 5 and 7, and there are no atmospherics of intensity 2. At 21 hours there is a tendency for the development of atmospherics of lower intensities and once again we find as at 22 hours, that 30% of atmospherics are confined to intensity 2, 50% to intensity 3 and only 20% to intensity 4. By this time the atmospheric activity has come down in magnitude from 124 to 41.

In Table IV are given the contributions to the total activity obtained from atmospherics of various intensities. Next to each number the percentage contribution is indicated in brackets.

TABLE IV

Classification of Atmospherics between 15 *and* 22 *Hours on the* 16*th August* 1940, *according to their Contribution to Total Activity*

Hour	Atmospheric activity contributed to the total activity by atmospherics of intensities. % contribution in brackets				Total activity
	2	3	4	5 and above	
15	2 (16)	3 (23)	8 (61)		13
16	10 (12)	60 (73)	12 (15)		82
17		27 (37)	48 (63)		75
18	2 (6)	18 (56)	12 (38)		32
19		18 (60)	12 (40)		30
20		24 (20)	88 (70)	12 (10)	124
21	4 (7)	18 (31)	36 (62)		58
22	8 (20)	21 (50)	12 (30)		41

This brings out more clearly the characteristics, not only of the process of building up of a thunderstorm as evidenced by the study of atmospherics but also the process of decay. The process of building up is accompanied by larger percentage contributions to the total atmospheric activity from atmospherics of higher intensities. The decay is evidenced by a decrease in this

percentage and a corresponding increase in the percentage contribution from atmospherics of lower intensities.

It is also noticed from Table II that at certain periods there is practically no change in atmospheric activity or a slight decrease but that later the activity suddenly increases. Two such cases are discussed here as typical examples.

The first example is taken from the 16th. As seen from Table IV, on the 16th between 18 and 19 hours there has practically been no change in activity (32 and 30) in spite of the fact that sunset occurred during this period. This seems to be contradictory to the invariable effect of sunset on atmospherics already described. But a little consideration shows that such is not the case. 16th is an exceptional day; thunderstorm activity reached a peak at 16 hours and from that time there has been a reduction in activity. At 18 hours activity is only 32. The first part of the Table shows that there is a tendency for atmospheric activity to decrease further but as actually observed there has been no change. We may therefore look upon sunset as being responsible for the preventing of a further decrease in atmospheric activity and also for providing the necessary conditions for bringing once more into being activity which attained a peak value at 20 hours.

The second example may be taken from the data for the 14th given in Table II. It is noticed that between 20 and 21 hours the atmospheric activity has remained unchanged ; but the distribution of the number of atmospheric according to intensities is 10, 3, 2 at 20 hours; 6, 6, 2 at 21 hours clearly indicates that there is a tendency for atmospheric activity to increase. As can be seen from Fig. 6, curve 11 *a*, there has been a gradual increase in activity through the night, the peak intensity being attained at 5 A.M.

3. *Short Wave Activity Preceding Activity on the Medium Waves.*—From an examination of curves 1, 2 and 3 (Fig. 4) it will be noticed that there is considerable atmospheric activity on the short waves during the afternoons, this being the strongest on the 20th, less on the 21st and least on the 23rd. It is also interesting to note that the atmospheric activity at 19 hours on the three days in Group 1, is also in the same order 80 on the 20th, 69 on the 21st and 51 on the 23rd. These facts taken together seem to suggest that probably the two phenomena are interrelated, the short wave activity being an indication of the coming into existence of conditions preparatory to the onset of a thunderstorm. Unless such conditions are already present before sunset, the trigger action of sunset described above may not give rise to such pronounced atmospheric activity.

The conditions preparatory to the occurrence of lightning in a thundercloud are the building up of powerful electric fields and the storing up of large quantities of electricity. The electric field strength at which the spark which we call lightning takes place in air at ordinary pressure is 30,000 volts per centimetre. In a thundercloud the pressure is lower and the presence of small drops of water introduces a new and important factor.

The building up of these high potential is explained in different ways by Wilson and Simpson (1920 and 1927). According to Simpson the generation of electricity is due to the disruption of rain drops by an air current stronger than it could face without instability. On this hypothesis the orders of magnitude of the meteorological and electrical quantities involved are shown to be in accordance with the observations of Schonland and Craib (1927) in South Africa.

Macky (1933) as a result of investigations on the deformation and breaking up of water drops in strong electric fields, found that when exposed to increasing fields a drop of radius r becomes elongated until at a definite field strength, given in volts/cm. by $F\sqrt{r} = 3875$, it becomes unstable and filaments are drawn out from the ends. When instability occurs a discharge passes through the drop in exactly the same manner as it would through a conductor pointed at both ends. The removal of water by the formation of filaments sets a limit to the size of the drops which can exist inside a thundercloud. Macky concludes that no drop larger than 0·15 cm. in radius can exist in the fully charged cloud and that the critical value of the field at which a breakdown occurs is of the order of 10,000 volts/cm. The splitting up of the drops and the building up of the high potentials thus seem to be accompanied by the occurrence of small local sparks.

The mechanism suggested by Wilson as the cause of the opposite charges on large and small drops depends upon the presence in the cloud of a number of slow ions. In the earlier stages of development of a charged thundercloud these may arise from natural sources, but later on they will be supplied in numerous numbers by brush discharges from water drops drawn out by the field into pointed forms (Schonland, 1932).

Starting therefore with a cloud having large drops, the occurrence of these local sparks indicate that the charge and potentials are building up rapidly. As was pointed out by Larmor (1938), the lightning discharge in a thundercloud could be expected to begin at a place of maximum electric force (not potential) and to force its way through the atmosphere without tearing it, initially along the direction of the force.

Further according to Clark Maxwell, in an electrostatic field the force cannot be a maximum in free space. He therefore concludes that discharges must be initiated most probably within the thundercloud. Thus the spark and brush discharges referred to above might prepare the way for the occurrence of lightning flashes in very small regions of the thundercloud, flashes of such small magnitude, compared with those met with in a regular thunderstorm, that they cannot be observed from the ground either visually or with the aid of a camera.

These flashes however may give rise to atmospherics. Norinder (1936) is of opinion that some types of atmospherics specially those classified as " clicks " have their origin from field variations caused by such local sparks and brush discharges. It is very likely that these atmospherics have characteristics different from those ordinarily radiated from lightning during thunderstorms.

Simpson (1929) suggested that there can be little doubt that the resistance of a fully developed lightning channel when most highly ionised may well be less than the critical value and the channel therefore able to oscillate. These oscillations are superposed on the main current. The thundercloud itself has distributed capacity and inductance and it is reasonable to assume as Laby Nicholls, McNeil and Nickson (1940) have done that the electrical discharge which radiates an atmospheric is a damped oscillation with a period determined by the instantaneous resistance, inductance and capacity.

As pointed out by Lutkin (1939) the resistance increases as the channel ionisation decreases, while capacity to earth and also inductance increase as the length of the channel increases. In the case of the local discharges referred to above, we might suppose that in view of the smallness of the capacity and inductance involved that the atmospherics which arise from these discharges are likely to be more prominent on the short waves. From curves 1, 2 and 3 (Fig. 4) it is seen that in the afternoon of the 20th, 21st and 23rd there is considerable activity on the short waves, with nothing at all in the medium waves. Taking along with this the fact that the trigger action of sunset is most pronounced on these days, the short wave activity may be considered as indicative of the building up of the conditions in the atmosphere necessary for the onset of a powerful thunderstorm. The onset is however prevented as explained earlier by the ionising influence of the sun, so that when the sun sets the storm bursts with all its violence.

If this view be correct, we must expect the setting of the sun to bring about a type of distribution of the number of atmospherics according to intensity on the 20th, 21st and the 23rd which is different from that observed

previously. The data abstracted here for convenience will illustrate this difference.

TABLE V

Classification of Atmospheric on the 20th, 21st and 23rd August 1940 according to Intensity

Date	Hour	No. of atmospherics of intensities				No. of Atm./min.	Atmospheric activity
		2	3	4	5		
20	18	1	1			2	5
	19	12	8	8		28	80
	20	7	9	7		23	69
21	18						
	19	12	11	3		26	69
	20	5	13	9	3	30	101
	21	4	9	8	9	30	112
23	18						
	19	15	3	3		21	51
	20	9	2	4		15	40

On the 20th just after sunset there are not only 12 atmospherics of intensity 2 but also 8 of intensity 3 and 8 of intensity 4. This is very unusual but later on with the progress of the storm the percentage of atmospherics of larger intensities increases with a corresponding diminution of those of smaller intensities.

The presence of a large number of atmospherics of large intensities is suggestive of the existence of a previous state of preparation and according to the explanation given above, this is clearly indicated by the short wave activity before sunset on these days.

The presence of the large number of atmospherics of intensity 2 (12 on the 20th and 21st, and 15 on the 23rd indicate that atmospheric activity is not confined to the particular centre which has already been prepared, but that there are other centres brought into action by the effect of sunset. The experimental results obtained by Schonland (1938) show that successive multiple lightning strokes may arise as a result of the existence of separate generating centres at different places within the cloud and that we can assume

that these larger thunder clouds may be expected to possess several such generating centres. When once such activity has been initiated, we find that as long as the activity is increasing there are a larger percentage of atmospherics of greater intensities as pointed out earlier.

It is quite clear from the above that on certain days atmospheric activity reaches very high magnitudes even after a short duration of half an hour from sunset. This building up of atmospheric activity to high magnitudes in such short periods leads to the conclusion that the setting of the sun acts like a trigger. Atmospherics are due to lightning flashes accompanying thunderstorms. Even when the meteorological conditions are favourable for the occurrence of a thunderstorm, still the storm itself does not usually commence until after sunset. The solar radiation by augmenting the leakage effects inside a thundercloud, prevents the attainment of the necessary critical potentials for the passage of the lightning flash. When sunset occurs, this restraining influence is removed and the thunderstorm bursts with all its violence. The evidence for the existence of these conditions appears to be indicated by the appearance of atmospherics on the short waves a few hours before sunset. The study of the activity on short waves therefore seems to provide information regarding the preparation of the atmosphere for the onset of a powerful thunderstorm a few hours before its actual occurrence and thus gives advance information about the meteorological condition of the atmosphere.

At the commencement of atmospheric activity it is usual to find a large percentage of atmospherics of low intensities and sometimes practically none of higher intensities. But in some cases a large number of atmospherics of higher intensities appear along with those of lower intensities. These seem to indicate that necessary conditions have already been built up and that atmospheric activity has been prevented from occurring by the action of solar radiation. Sunset therefore brings about atmospherics with large intensities. As these occurred only on those days when atmospheric activity on the short waves was noticed during the previous afternoons, this lends additional support to the view that the study of activity on the short waves will be able to provide useful advance information regarding the meteorological condition of the atmosphere.

Thus it is evident that the study of atmospheric activity on the short waves simultaneously with those on medium waves will give results which would supplement each other and provide the necessary basis for correlating the nature of the observed atmospherics with meteorological conditions, which is the main purpose of the present investigation. The data collected during the half year July to December 1940 are being examined and the results will be published later.

A study of the curves reveals further that on those days on which the trigger action of sunset is most pronounced, the peak activity is reached very early in the night (about 8 P.M.), whereas on those days on which the trigger action of sunset is not so pronounced, the rate of growth of thunderstorm activity is slow and the peak activity is attained very much later in the night (between 10 P.M. and midnight).

Atmospherics and Meteorological Depressions.

Before concluding, a few observations may be recorded which, though they have no direct relation to the subject of the present paper, are likely to be of some importance to the main object of the investigation. It will be seen from the curves given in Figs. 4, 5 and 6 that atmospheric activity has been most intense at particular times on particular days. Observations made by the " Challenger " showed that the frequency of thunderstorms at sea had a pronounced maximum between 2 P.M. and 4 A.M., while the occurrence of lightning only showed a maximum between 8 P.M. and 10 P.M. Over land, heat thunderstorms occur during the afternoons but certain types of thunderstorms associated with the line of separation between warm and cold current show no preference to any hour of day or night.

Maxima of atmospheric activity on the medium waves are attained in the early morning on the following dates : 15, 16, 18, 21 and 24. On most of these days, however, there has been practically no activity on the short waves. But from the afternoon of the 20th till the morning of the 22nd there has been almost continuous short wave activity. Whether this prolonged activity on the short waves is indicative of " the unsettled condition off the Circars' coast ", reported in the *Indian Daily Weather Report* dated 19th August 1940, and whether the occurrence of a peak activity on the medium waves in the early hours of the morning of the 21st along with severe short wave activity is indicative of the fact that " the unsettled conditions off the Orissa Coast developed into a depression", as reported in the *Indian Daily Weather Report* of the 21st August 1940, is a matter which requires to be studied in detail. Further data are being collected and results will be published in due course.

Summary

The paper describes the results of observations on the nature of the Effect of Sunset on Atmospherics. An automatic device specially constructed for the purpose was employed and with its aid, records of atmospherics on two wavelengths (37·5 metres and 375 metres) were taken for about two minutes at intervals of one hour throughout the day.

The study has brought to light certain interesting features characteristic of the period of investigation, which extended for a fortnight in the month of

August 1940 and showed active monsoon conditions, particulaly between the the 11th and the 26th, in the Peninsula, the central parts of the country and North West India (*India Weather Review*, August 1940).

It is pointed out that (1) the effect of sunset on atmospherics is that of Trigger action, (2) the study of atmospherics can give advance information regarding the preparation of the atmosphere for the onset of a powerful thunderstorm and (3) prolonged atmospheric activity on the short waves appears to be connected with the formation of meteorological depressions.

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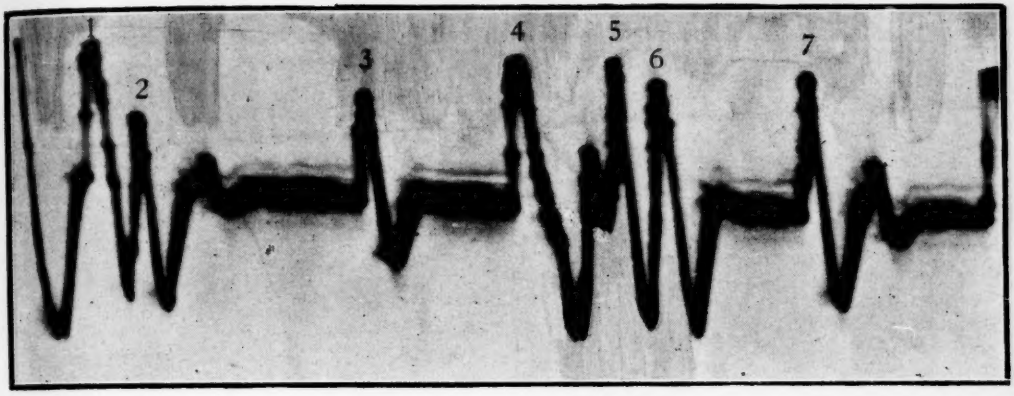

FIG. 1

Enlargement of a section of the record of atmospherics taken at 11 p.m. on 8-10-1934

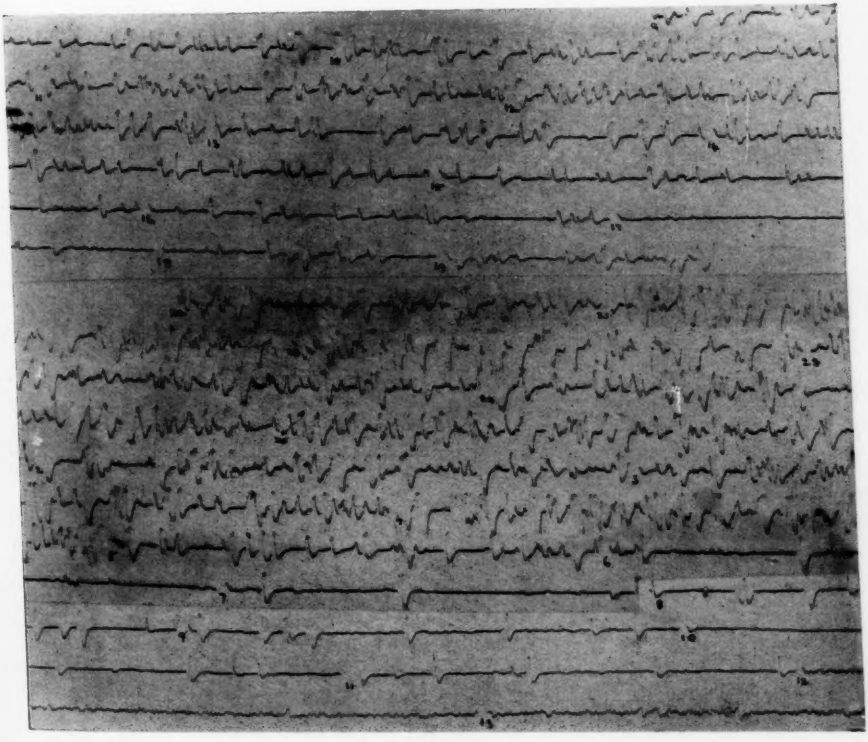

FIG. 2

Record of atmospherics from 9 hours on 17-8-1940 to 13 hours on 18-8-1940